STRUCTURAL AND PREPARATIVE STUDIES OF SOME PHENYL DERIVATIVES OF GROUP IV A ELEMENTS

A THESIS

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A C K N O W L E D G E M E N T S

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C O N T E N T S

ABSTRACT

The infrared spectra of a number of aryl tin and aryl le compounds have been examined in the 2-50 μ. region. The infrared spectra (2-15 μ.) of these derivatives are the spect of mono-substituted benzene derivatives. The spectra in the far infrared region (15-50 μ.) have been found to be distinct and can be used for the qualitative identification of these compounds. Frequency assignments are made and the spectra a discussed in terms of structural features of the organometall derivatives. There seems to be no evidence to support the possible existence of Ph_3Sn^+ and Ph_3Pb^+ cations in any of the derivatives examined. The derivatives with strong electro-negative groups, i.e. fluorides, fluoroborates, perchlorates, hexafluoroarsenates, hexafluoroantimonates, nitrates are considered as predominently covalent in character with polyme structures involving five co-ordinate tin or lead atoms. A number of new compounds have been prepared during the course of this work.

Conductivity measurements have been made on nitromethane solutions of hexaphenylditin and hexaphenyldilead at varying temperatures. It has been conclusively shown that there is n heterolytic dissociation of these compounds.

The far infrared spectra (15-50 μ.) of a range of aryl compounds of Group IVA, VA, VIA and VIIA elements have been studied. Frequency assignments are made for the stronger ban Most of the vibrational frequencies occurring in this region

sensitive to the substituent atom attached to the benzene rin

Some new salts of the triphenylmethyl carbonium ion have been prepared and their infrared spectra examined.

The carbonium ion dyestuffs (malachite green, brilliant green and crystal violet) form ionic derivatives with fluoroborate, perchlorate and heteropoly acid anions. The solution spectra of these derivatives have been examined in the visibl region (400-700 m.μ.) and the spectra are discussed in terms of aggregation of the dyestuff cations in solution. Many new crystalline compounds have been prepared with fluoroborat perchlorate and heteropoly acid anions and the infrared and reflectance spectra discussed.

The cyanide , cyanates, thiocyanate, metaborate and sulph derivatives of the dyestuffs have been found to be covalent with a true tetrahedral arrangement about the central carbon atom.

The dyestuffs give orange-red solutions in strong acids. The colour is due to the formation of new species by protonat of the nitrogen atoms of the dyestuff cations. Many new salt containing these protonated species with anions derived from heteropoly and Lewis acids have been prepared and examined spectroscopically.

The dyestuffs also form complexes with Lewis acids ($SnCl_4$, $SbCl_5$) in non-aqueous solvents. The successive addi of $SbCl_5$ has been studied and a number of new complexes have been prepared with crystal violet.

CHAPER I

THE INFRARED AND FAR INFRARED SPECTRA OF ORGANOTIN COMPOUNDS

Introduction

Many of the observed properties of the organometallic compounds of the Group IVA elements are similar. All these elements have four valency electrons with a s^2p^2 configuration in their ground states. The two electrons in the subshell have coupled spins and in this state only two unpaired p electrons should be available for bonding. In the more usual four covalent state, one of the s electrons is promoted to a higher energy level and tetrahedral sp^3 hybridisation occurs. Because of the sp^3 hybridisation and the presence of an octet of electrons, all the organometallic compounds in their four covalency state are relatively stable and possess relatively low chemical activity. The marked stability of R_4Sn (R = alkyl or aryl) compounds over R_2Sn type of compounds demonstrates the effect of increased hybridisation and also inert gas electronic structure. However, among these elements there are also differences which in some cases lead to the rather widely different chemical properties of their organometallic compounds. There is a considerable difference in electronegativity values of carbon and the other elements of Group IVA elements. The Pauling electronegativity values are given in Table I.

TABLE I

Element	Pauling's scale of electronegativities
C	2.5
Si	1.8
Ge	1.7
Sn	1.7
Pb	~

From the decrease in electronegativities, the metal-carbon bonds are expected to have some ionic character. (Luijten and Van Der Kerk[1]). In compounds of the type R_3MX (R = alkyl, M = metal, X = halogen) the percentage of ionic character for the M-X bonds derived from differences in electronegativity are shown below.

TABLE 2

Bond	Difference in electronegativity	% ionic
C-Cl	0.5	6
Si-Cl	1.2	30
Ge-Cl	1.3	35
Sn-Cl	1.3	35
Pb-Cl	~	~
K-Cl	2.2	70

With decreasing electronegativities (Table I), an increase in the polar character of the M-X bonds is evident as illustrated by Table 2.

The carbon atom is in a special situation within the group. Since it is a second-period element it cannot expand the valency shell beyond eight electrons. For silicon and other elements in the higher periods such expansion is not forbidden and may account for some of the differences between the chemistry of these elements and that of carbon. Although the elements of this group, with the exception of carbon, show no tendency to form double bonds of the ethylenic type i.e. $p_\pi - p_\pi$, there is strong evidence that the d-orbitals of the elements other than carbon are used for $d_\pi - p_\pi$ bonding. Chatt and Williams[2] have studied the thermodynamic dissociation constants of four acids of the type $p\text{-}R_3MC_6H_4COOH$ where M represents carbon, silicon, germanium or tin. Carbon is the most electronegative of the four elements and it should enhance the acid strength to the greatest extent. Actually the carbon compound shows the lowest acid strength and this is taken to indicate that $d_\pi - p_\pi$ bonding is operative in the other three compounds. A schematic representation of the orbitals forming the $d_\pi - p_\pi$ bonding of the $M\text{-}C_{aryl}$ bond for a silicon compound is shown in Figure I. This type of bonding compensates for the increasing inductive effect in going from silicon to lead. The infrared and ultraviolet spectra of phenyltin compounds have been interpreted (Griffiths and Derwish[3]) on the basis of the $Sn\text{-}C_{aryl}$ bond having some double bond character. These findings

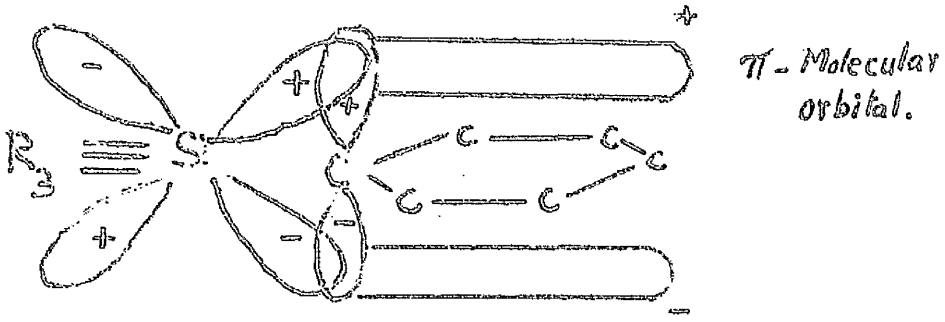


Figure I. π-bonding between silicon and an aromatic ring system. Chatt and Williams[2].

are further discussed by a theoretical predication made by Craig, Maccoll, Nyholm, Orgel and Sutton[4]. Several other examples of this type of multiple bonding involving d-orbitals are listed in a survey in which the behaviour of silicon is examined in detail. (Stone and Seyferth[5]).

Among the elements of this group there are some properties that are characteristic of one element only. The most unusual property of the organotin compounds is the ionisation of the R_3SnX and R_2SnX_2 type of compounds. They are not ionised as R_3Sn^+ or R_2Sn^{2+} but co-ordinated with water as $R_3Sn(OH_2)^+$ or $R_2Sn(OH_2)_n^{2+}$. The dissociation of the organotin halides R_3SnCl (where R=alkyl or aryl) in the presence of an electron donor compound has been generalised[6,7].

$$R_3SnX + :Y \rightleftharpoons R_3SnY^+ + X^-$$

The R_3SnY^+ species may or may not undergo subsequent reaction.

e.g. proton transfer if Y is H_2O:

$$R_3Sn(OH_2)^+ + H_2O \rightleftharpoons R_3SnOH + H_3O^+$$

The extent of this type of reaction depends on the nature of both the R and the Y group. Similarly, dimethyltin dichloride dissociates almost completely in water[8,9].

$$(CH_3)_2SnCl_2 + nH_2O \longrightarrow (CH_3)_2Sn(OH_2)_n^{++} + 2Cl^-$$

The resulting solutions are acidic due to further hydrolysis of the cationic species formed in the above reaction.

$$(CH_3)_2Sn(OH_2)_n^{2+} + H_2O \rightleftharpoons (CH_3)_2Sn(OH_2)_{n-1}OH^+ + H_3O^+$$

The degree of hydrolysis depends on the concentration of the solution.

In all the above reactions of dissociation and hydrolysis, it is considered that the tin atom is present in penta or higher co-ordination state in the organotin cationic species formed in solution. This characteristic feature of penta or hexa co-ordinate tin atom has been shown in several previous reports[10-14].

Conductivity measurements on alkyltin halides have shown that these compounds are not true electrolytes in the solid state, but when dissolved in methyl or ethyl alcohol, water, pyridine, or acetone they are relatively good conductors; whilst in benzene, ethyl ether, nitrobenzene or nitromethane they are poor conductors (6,10,15-18). These compounds have ordinarily been looked upon as salts as they exhibit the above properties which are similar to those of salt-like

substances.

Early workers placed more emphasis on synthetic methods than on physical-chemical studies of these compounds. This is reflected by the absence of any detailed information on the infrared spectra of organotin compounds, the only exception being tetramethyltin[19-23] and tetraphenyltin[24-26]. Within the last few years, however, spectra have been reported for a fairly wide range of alkyl and aryl tin derivatives[27,28,30]. The main reason for studying the infrared spectra of the organotin compounds is to obtain information regarding the structural features of these compounds. Although Ph_3M^+(M=C, Si, Ge, Sn, Pb) derivatives are well known for M=C. (See chapter on Carbonium Ions), there have been doubts about the existence of Ph_3Si^+, Ph_3Ge^+, Ph_3Sn^+ or Ph_3Pb^+ ions. The compound R_3SiCl reacts with silver perchlorate to give trialkyl or triaryl silicon perchlorates but the evidence on the bonding in these compounds is not complete. They react in solvolytic reactions as if they were ionic but their infrared spectra are not definitely in favour of either a covalent or an ionic structure for these products. However, Ph_3Si^+ has recently been reported in the salt Ph_3SiSbF_6, but it could be covalent as found by Clark and O'Brien[29] for Me_3SnSbF_6. As regards the tin compounds contradictory statements[52-55] have been made about the probable existence of Me_3Sn^+ or Ph_3Sn^+ ions.

The present work was undertaken to investigate by infrared

spectroscopy the probable existence of Ph_3Sn^+ ions in the aryltin compounds. After the completion of the major part of this work, a number of workers[27,28,30] reported infrared investigations on the structure of phenyltin derivatives. Although some of the compounds studied by these workers were different from those studied here, their results are in complete agreement with those of the present work, and they have reached the same conclusions. The examination of the infrared spectra of these compounds supports the recent view [29,53-55,89,91] that the organotin derivatives are covalent rather than ionic compounds. There is little evidence for the existence of Ph_3Sn^+ or Me_3Sn^+ cations in any of the known organotin compounds. The present work includes infrared studies on a wide range of phenyltin compounds, and some alkyltin derivatives. A few of these compounds are new materials and others were prepared by standard published procedures. The infrared and far infrared spectra of the compounds have been examined over the range 5000-200cm^{-1} (2-50μ.). The absorptions are discussed and assignments are made for the infrared vibrations involving the tin atom in combination with other atoms. The structures of phenyltin halides, tetrafluoroborate, perchlorate, hydroxide, oxides and acetates are discussed in detail.

The infrared spectra of aryltin compounds

All the phenyltin compounds show quite similar infrared spectra in the sodium chloride region(2-15μ) but beyond 15 μ. they are characteristic and this region is particularly useful for the qualitative identification of these compounds.

In considering the spectra of these compounds, there are two possible approaches. The molecule can be considered as a whole and this would lead to a very complex description. Alternatively, the spectra can be split into bands which result from the organic part of the molecule and those which result from vibrations of the central organometallic skeleton.

The most complete previous treatment being that of Kriegsmann and Geissler[30] who have used the latter approach to explain the spectra of some alkyl and aryl tin derivatives.

For a compound of the type R_3MX, (R=akyl or aryl group, M=Si, Sn or Pb, X=anionic group). Kriegsmann and Geissler[30] divide the vibrational modes into these two types as above and this device will be followed here. These modes are.-

(i) Vibrations of R (Benzene ring):- In the case of phenyl derivatives, the vibrations are those of mono-substituted phenyl derivatives.

(ii) Skeletal vibrations of the group R_3-M-X:- Since R is alkyl or aryl group, these vibrations are formally of the groups C_3-M-X and there are corresponding groups

C_2MX_2 and CMX_3 for di- and mono-phenyl derivatives respectively. The M-X vibrations normally occur in the far infrared region below 400 cm^{-1}. The assignements for these modes are made by analogy with previously reported M-X vibrations for the tin compounds.

The Ring Vibrations:- The most comprehensive survey of the infrared and Raman spectra of mono-substituted phenyl derivatives is by Whiffen[31].

A mono-substituted benzene ring is of C_{2v} symmetry and would have thirty fundamental vibrations i.e. 11 of symmetry A_1, $10B_1$, $3A_2$, and $6B_2$.

It is more convenient to discuss these frequencies in terms of the approximate description of the normal modes rather than to take each symmetry class respectively. Three of the fundamental frequencies are of species A_2 type and hence are forbidden in the infrared spectrum. The remaining twenty-seven are infrared active. Of the thirty vibrations mentioned above, only six appear to be sensitive to the nature of the substituent atom. Five of the fundamental vibrations of a simple mono-substituted benzene occur in the far infrared region (650-200 cm^{-1}). Although the phenyltin compounds are not of overall C_{2v} symmetry, the departure of a phenyl ring system from C_{2v} symmetry is not great. Therefore, Whiffen's[31] assignments for the mono-substituted benzene ring system are accepted and his nomenclature will be followed in

the following discussion. The approximate mode diagrams (Randle and Whiffen[32]) for the vibrations of a mono-substituted benzene group are shown in Figure 2. The assignments for the fundamental vibrational frequencies of C_6H_5X(where X = substituent) are made in Tables (3-6) for all the phenyltin derivatives studied in the present work. In the first column of each Table is given Whiffen's notation for the modes of vibrations of a mono-substituted benzene group. A complete frequency assignment analysis of phenyl group vibrations is shown in Figure 3 for tetraphenyltin which could be considered as a representative member of all the phenyltin derivatives studied in the present work.

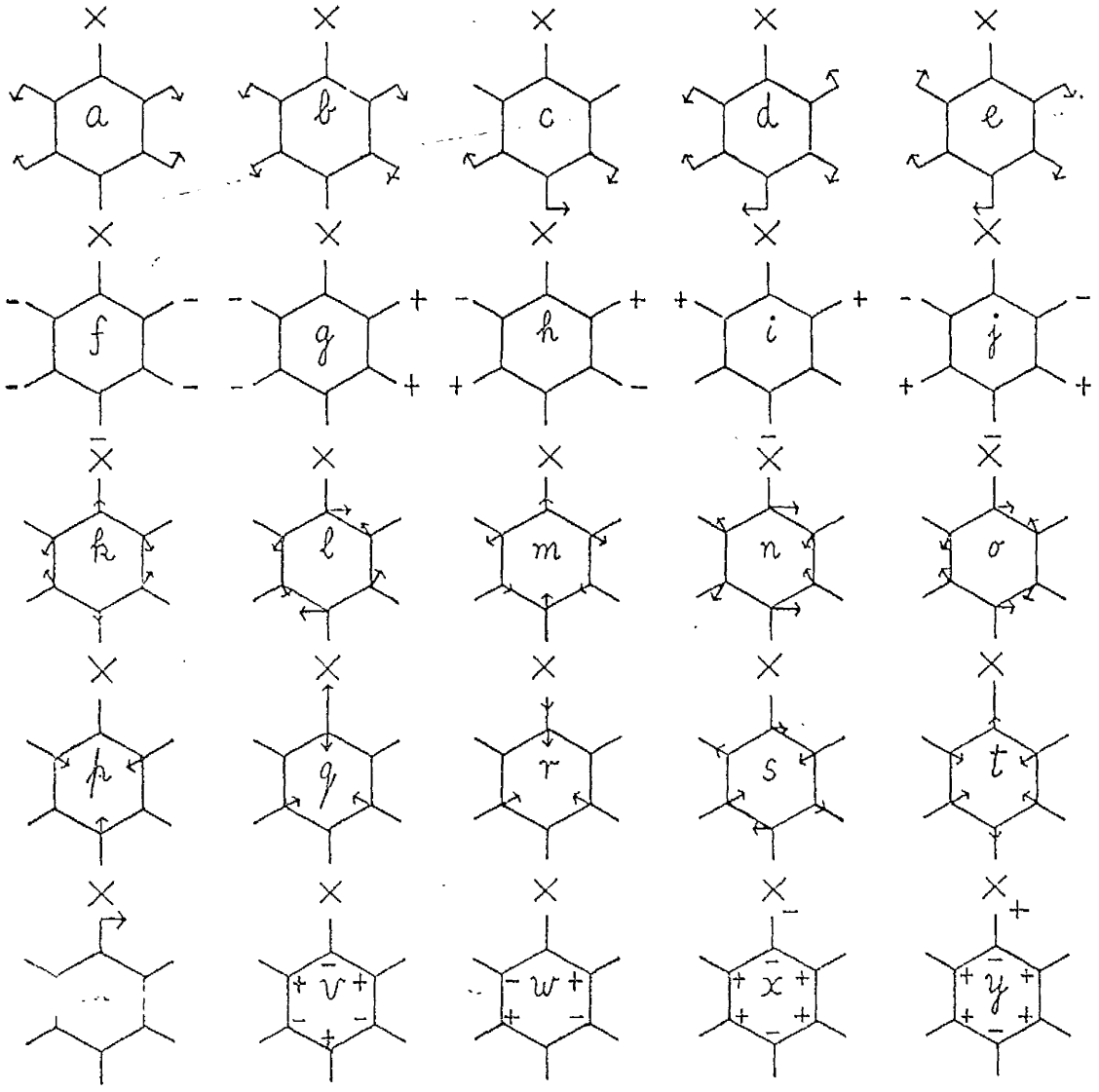


Fig. 2

Fundamental vibrations of C_6H_5X (Whiffen[31])

Discussion

The 3070-1650 cm^{-1} region:- There are essentially five C-H stretching modes for each compound whose frequencies must lie in the range 2950-3120 cm^{-1} by analogy with other aromatic C-H frequencies (Bellamy[33]). Kriegsmann and Geissler[30] have observed these modes in the 3070-3010 cm^{-1} region in the study of some phenyltin compounds. In all the phenyltin derivatives, a weak to medium band is observed around 3040 cm^{-1} which is identified with Whiffen's 'z' band for a stretching vibration. In general the spectra are not well resolved in this region as a spectrophotometer with high resolving power would be needed to get a good resolution. The overtones and combination bands of the C-C normal modes occur in the 200-1650 cm^{-1} region as four to five weak intensity absorption bands.

The region below 1650 cm^{-1}:-

The band near 1475 cm^{-1}:- This band has been assigned to a C-C stretching mode by Griffiths and Derwish[34] for their four phenyltin compounds. In the purely organic compounds studied by Katritzky and Lagowski[35] the range 1511-1477 cm^{-1} was found for this band and it was noted that with heavier substituents in the benzene ring, the 1475 cm^{-1} band was found at the lower frequency end of the range. Amster and Colthup[36] have observed a band at 1480 cm^{-1} in phenyl phosphine derivatives and they have attributed this absorption to a C-C normal mode and assigned it as Whiffen's 'm' band of the mono-substituted phenyl group vibrations. A similar absorption within the range

1480-1468 cm^{-1} was recorded by Poller[27] for a number of phenyltin derivatives and has been assigned to a C-C stretching mode. In the present work, a medium to strong intensity band within the range 1478-1471 cm^{-1} was shown by all the phenyltin compounds. This band is assigned as Whiffen's 'm' band for the mono-substituted benzene group vibrations.

The band near 1425 cm^{-1} (Whiffen's 'n' band). A very sharp intensity band is recorded in the range 1430-1425 cm^{-1}. With the exception of the C-H out-of-plane vibrations (at 750-670cm^{-1}) this band is the most intense of the benzene ring bands. The band is assigned to another C-C stretching mode by Griffiths and Derwish[34] who have assigned the corresponding absorption at 1435-1434 cm^{-1} to this vibration. Katritzky and Lagowski[35] have given the range 1447-1446 cm^{-1} for mono-substituted benzenes with a heavy atom substituent. This absorption was originally recorded at 1429 cm^{-1} by Young et.al.[37] for phenyl silicon compounds and it has been shown to occur (Henry and Noltes[38]) at the same frequency in the corresponding phenyl germanium and lead compounds. In the present work this band is assigned, as Whiffen's 'n' band, to a C-C stretching mode.

The band near 1370 cm^{-1}:- A weak intensity band is observed in the range 1376-1370 cm^{-1} in all the compounds except in the phenyltin acetates (where it is masked). An absorption has been reported at 1374 cm^{-1} for Chlorobenzene and it was assigned to be a summation frequency (i+y) by Whiffen[31]. The range of this summation frequency has been quoted at 1381-1377cm^{-1} by Herzfeld, Ingold, and Poole[39]. By comparison with the above

Table 3 — Fundamental Vibrational frequencies of C_6H_5I

Mcdo		Vibrational frequency of C_6H_5X (cm^{-1})		
Whiffen's Notation	Description	Ph_4Sn	$Ph_3Sn-SnPh_3$	Ph-Sn-Ph
z	$A_1\gamma$ C-H	3040m	3040m	3035w
m	$A_1\gamma$ C-C	1475s	1473s	1471s
n	$B_1\gamma$ C-C	1425vs	1425vs	1425s
		1376w	1370w	1370w
o	$B_1\gamma$ C-C	1332w	1326w	1325w
e	$B_1\beta$ C-H	1299w	1295w	1292w
		1253w	1252w	1250w
a	$A_1\beta$ C-H	1176w	1185w	-
c	$B_1\beta$ C-H	1149w	1149w	1156w
d	$B_1\beta$ C-H	1070vs.1058sh.	1070vs.1058sh.	1064m
b	$A_1\beta$ C-H	1021m	1020m	1015m
p	A_1 ring	997m	997s	994m

Table 3 (continued)

Fundamental Vibrational frequencies of C_6H_5X

Mode		Vibrational frequency of C_6H_5X (cm^{-1})		
Whiffen's Notation	Description	Ph_4Sn	$Ph_3Sn-SnPh_3$	Ph-Sn-Ph
j	B_2 Y C-H	985w	-	-
i	B_2 Y C-H	910w	909w, 829w	-
f	B_2 Y C-H	728vs	728vs	721s
v	B_2 Y C-C	697vs	696vs	693s
s	B_1 a C-C-C	618w	-	-
y	B_2 X sens.	455vs, 448vs	452sh, 442vs	448sh, 442s
t	A_1 X sens.	263vs	260b	277w

-absorptions not observed or obscured.

Table 4 — Fundamental Vibrational frequencies of C_6H_5K

Mode		Vibrational frequency of C_6H_5K (cm^{-1})				
Whiffen's notation	Description	Ph_3SnF	Ph_3SnCl	Ph_2SnCl_2	$PhSnCl_3$	Ph_3SnBr
z	$A_1\gamma$ C-H	3040m	3035m	3045s	3050m	3030m
m	$A_1\gamma$ C-H	1475m	1473s	1475s	1471s	1472s
n	$B_1\gamma$ C-C	1429s	1429s	1430vs	1425vs	1426vs
		1370w	1374w	1376m	1370w	1372w
o	$B_1\gamma$ C-C	1332w	1330m	1332s	1326s	1330s
e	$B_1\beta$ C-H	1300w	1300m	1299s	1299w	1299m
		1255w	1258w	-	-	1256w
a	$A_1\beta$ C-H	-	1185w	1190w	1188w	1188w
c	$B_1\beta$ C-H	1149w	1155w	1162w	1155w	1151w
d	$B_1\beta$ C-H	1076w	1073s	1070vs	1070s	1071vs
b	$A_1\beta$ C-H	1021w	1018m	1018s	1019m	1018s

Table 4
(continued)

Fundamental Vibrational Frequencies of C_6H_5Y

Wilfen's Notation	Mode Description	Ph_3SnF	Ph_3SnCl	Ph_2SnCl_2	$PhSnCl_3$	Ph_3SnBr
p	A_1 ring	997m	994s	995s	995s	997s
j	B_2 C-H	-	970w	970w	-	970w
i	B_2 C-H	917w	917w	917w	913w	919w
i'	B_2 C-H	1272s,1275sh.	1284s	1284s	1310s,1294s	1272s,1284s
A	B_2g C-C	999s	1004s	1004s	1001s,998s	1004s
s	B_1 C-C-C	-	-	-	-	-
y	B_2X sens.	1452s,1478sh.	1448s,1458sh.	1454s.	1435s	1438s,1423sh.
t	A_1X sens.	278s	268s.	278m	270m	267s(Sn-Br)

Table 5 Frequency assignments of Ph_3SnOH and $(Ph_3Sn)_2O$.

Mode		Absorption frequencies cm^{-1}	
Whiffen's notation	Description	Ph_3SnOH 3610w (ν_sOH)*	$Ph_3Sn-O-SnPh_3$
z	A_1 νC-H	3030m	3045m
m	A_1 νC-C	1477m	1475m
n	B_1 νC-C	1425s	1425s
		1370w	1371w
o	B_1 νC-C	1325w	1330w
e	B_1 βC-H	1292w	1295w
		125dw	1258w
a	A_1 βC-H	1183w	1183w
c	B_1 βC-H	1149w	1149w
d	B_1 βC-H	1075s	1070vs

Table 5 Frequency assignments of Ph_3SnOH and $(Ph_3Sn)_2O$.
(continued)

Mode		Absorption frequencies cm^{-1}	
Whiffen's notation	Description	Ph_3SnOH 3610w (ν_sOH)*	$Ph_3Sn-O-SnPh_3$
b	A_1 βC-H	1020m	1020m
p	A_1 ring	995m	990s
j	B_2 γ C-H	979w, 963w	-
i	B_2 γ C-H	909m	918w, 912w
		898s(δOH)*	774vs(ν_{as}Sn-O-Sn)*
f	B_2 γ C-H	730sh, 720vs	729vs, 723sh
v	B_2 ØC-C	690vs	699sh, 693vs
s	B_1 αC-C-C	615w	-
y	B_2 X sens.	444s.b.($\nu_{as}SnPh_3$)*	455sh, 441s.b.($\nu_{as}SnPh_3$)*
t	A_1 X sens.	270b.	268b.

* These assignments are made according to Kriegsmann and Geissler[30].

Table 6 — Frequency assignments of Phenyltin acetates

Mode		Absorption frequencies cm^{-1}.		
Whiffen's assignment	Description	$Ph_3SnOOCCH_3$	$Ph_3SnOOCCF_3$	$Ph_2Sn(OOCCF_3)_2$
z	A_1 ν C-H	3035s	3050w	3049m
			1656s(C-O)	1670sh(C-O)
			1645vs(C-O)	1645vs(C-O)
		1565sh	1565sh	
		1534vs(C-O)		
m	A_1 ν C-C	1478m	1477m	1475m
			1445w(C-O)	
n	B_1 ν C-C	1430vs	1429vs	1429vs
		1410sh(C-O)		
o	B_1 ν C-C	1340w	1333w	1333w
e	B_1 βC-H	1300w	1299w	1299w
a	A_1 βC-H	1190w	1190vs(C-F)	-
			1195vs(C-F)	1198vs(C-F)

Table 6 (continued)

Frequency assignments of Phenyltin acetates

Mode			Absorption frequencies cm^{-1}		
Whiffen's assignment	Description		$Ph_3SnOOCCH_3$	$Ph_3SnOOCCF_3$	$Ph_2Sn(OOCCF_3)_2$
				1163m(C-F)	
c	B_1	βC-H	1149w	1149m	-
d	B_1	βC-H	1075vs	1073s	1074m
b	A_1	βC-H	1020s	1020m	1020w
p	A_1	ring	998m	995m	995w
				846s	847m
				801w	805m
				792s	787m
f	B_2	γC-H	732vs	725vs	738sh.725vs
v	B_2	δC-C	698vs	697s	694s
s	B_1	C-C-C	-	619w	-
y	B_2	X sens.	453s,b.	452.s.b.444sh.	455s.b.446sh
t	A_1	X sens.	270b	267b	278-265b

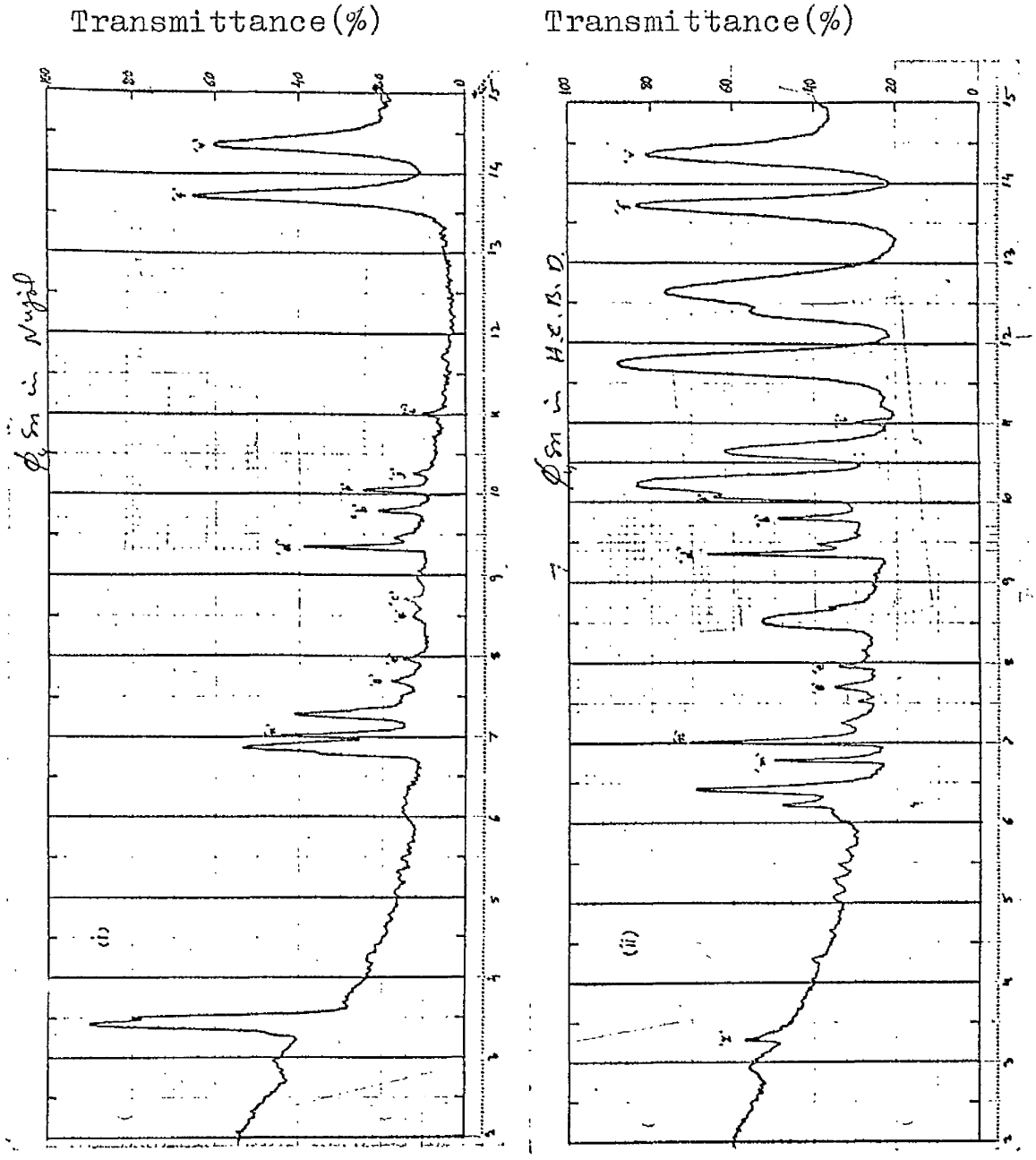


Fig. 3(a) Infrared spectra of tetraphenyltin
(i) in Nujol mull (ii) in hexachlorobutadiene mull.

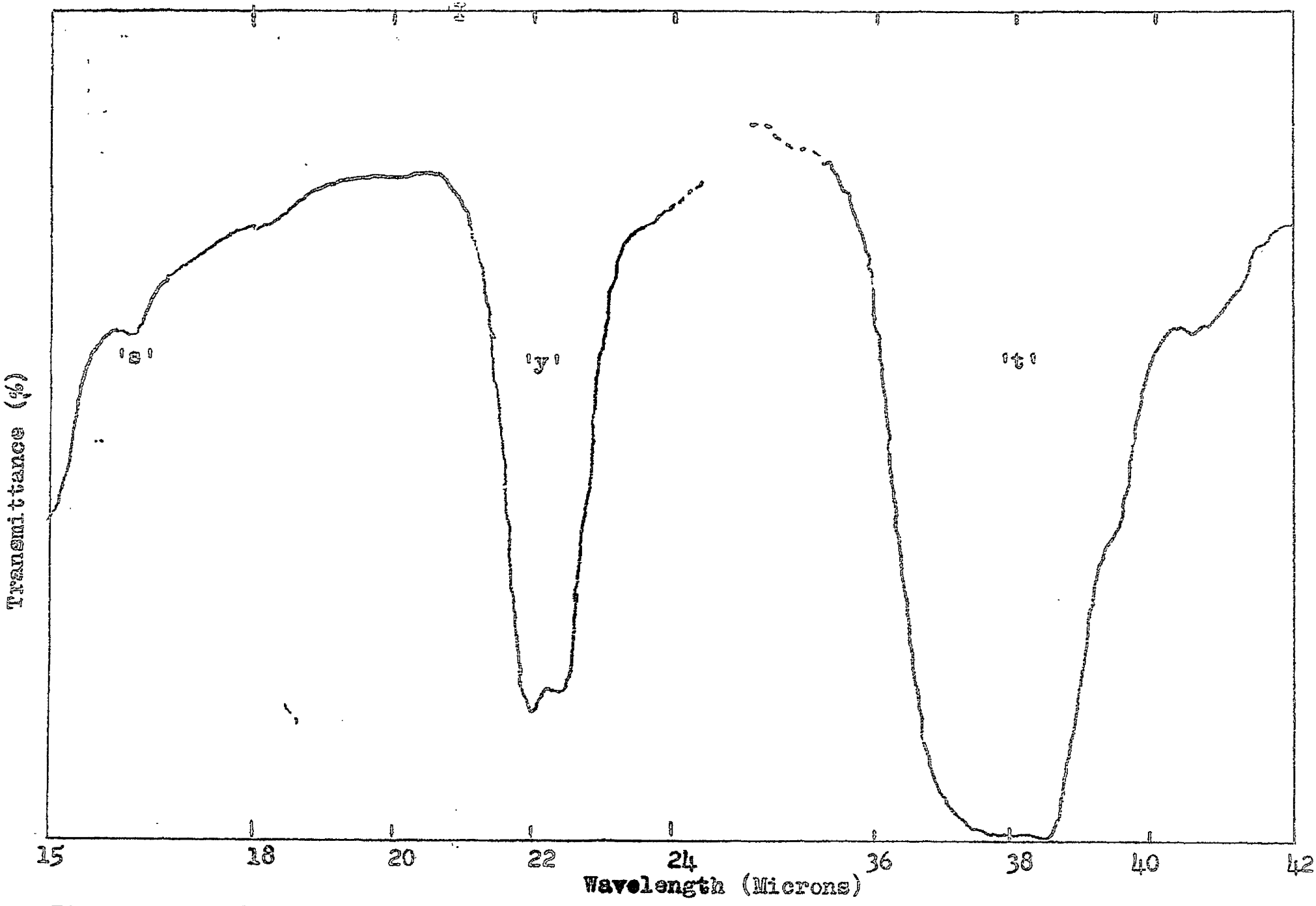


Figure 3 b. Far infrared spectrum of tetraphenyltin

values, this band is assigned as a summation frequency.

The 1340-1250 region:- There are three weak to medium intensity bands which are observed in almost all cases in the 1340-1325, 1300-1292 and 1258-1250 cm^{-1} ranges. However, it is difficult to quote with certainty the corresponding ranges observed by Griffiths and Derwish[34] because they used a very high resolution intrument and they have also detected other weak bands in this region. The ranges for their compounds are probably 1337-1334, 1305-1304 and 1267-1262 cm^{-1}. No mention is made by Bellamy[33] or by Katritzky and Lagowski[35] of benzene ring absorptions in this region. Poller[27] has observed three bands, weak to medium intensity, around 1300 cm^{-1} in the study of infrared spectra of phenyltin compounds. He has assigned these bands as benzene ring absorptions. In the present work the bands at 1330 cm^{-1} and at 1300 cm^{-1} are assigned as Whiffen's 'o' (γ C-C) and 'e' (β C-H) bands of the phenyl groups. Lack of any strong evidence, however, prevents the assignment of the band at 1255 cm^{-1} to β C-H.

The 1200-1100cm^{-1} region:- There are two bands usually of weak intensity which occur in this region at 1190-1176cm^{-1} and at 1162-1149 cm^{-1}. These bands are masked in phenyltin trifluoroacetates because of the C-F absorption bands. Of the compounds examined by Katritzky and Lagowski[35] generally only those compounds with electron donating substituents in the benzene ring absorbed in this region, and the ranges quoted are 1181-1070 cm^{-1} and 1160-1150 cm^{-1}. Both of these bands are assigned to β C-H in-plane deformation modes by Randle and

Whiffen[32]. According to Amster and Colthup[36] for phenyl phosphine compounds, the absorptions at ca 1180 cm^{-1} and at 1157 cm^{-1} are assigned as Whiffen's 'a' and 'c' bands associated with β C-H vibrations. Thus by analogy, in the present work, the bands near 1185, 1155 cm^{-1} are identified as βC-H vibrations and they are assigned as Whiffen's 'a' and 'c' bands respectively.

The 1070 cm^{-1} band:- (Whiffen's 'd' band). This is a very sharp band occuring in the range 1076-1064 cm^{-1} in all the compounds. This band has been observed in the spectra of mono-substituted benzenes by a number of workers[32,34] and assigned to a βC-H in-plane deformation vibration. The absorption is much more intense when the substituent in the benzene ring is a metal atom. Henry and Noltes[38] have examined the spectra of some phenyl-, phenylallyl- and phenyl-vinyltin compounds and they have shown that a band at 1065 cm^{-1} is characteristic for the phenyltin group and it undergoes displacement in the analogous silicon, germanium and lead compounds. These frequency shifts as recorded in the present work, are shown in table 7.

The band is believed to be a perturbed phenyl vibration, probably a C-H in-plane deformation vibration (Whiffen[31]) which shifts to lower frequency with the increasing atomic weight of the central atom. Thus, this band has been found to be of great value in recognising the phenyl derivatives of Group IV elements. The present work shows that substituents on the

Table 7

Compound	Absorption frequency cm^{-1}
Tetraphenylsilane	1100
Tetraphenylgermane	1080
Tetraphenyltin	1065
Hexaphenylditin	1065
Diphenyltin	1064
Tetraphenyl lead	1052

tin atom can also cause slight variations in the frequency of this band but overlapping with the phenylgermanium band ($1080cm^{-1}$) and the phenyllead band ($1052\ cm^{-1}$) is not likely to occur. The characteristic phenyltin band ($1065\ cm^{-1}$) shows a remarkable decrease in intensity in the case of the acetates and trifluoro-acetates and this could lead to difficulties in using the band to identify a phenyltin derivative.

The $1025-900\ cm^{-1}$ region:- Three or sometimes four bands, usually of weak or medium intensity, occur in this region. All the compounds show a medium intensity band in the range of $1025-1014\ cm^{-1}$ which is assigned to a β C-H in-plane deformation mode[32,34]. Another strong to medium intenstity band is shown within a narrow range $999-996\ cm^{-1}$ by all the aryltin compounds. This band is assigned as Whiffen's 'p' band associated with the symmetric ring mode. It should be noted here that this absorption was not shown by all the compounds examined by Katritzky and Lagowski[35] and they have reported a much greater variation in the absorption frequency of this band ($1007-990cm^{-1}$) than is found in the present work.

The remaining two absorptions at ca 980 cm^{-1} and at 910 cm^{-1}, which are relatively much weaker in intensity and sometimes are not observed in the spectra of some of these compounds, are assigned as Whiffen's 'j' and 'i' bands for γ C-H modes of vibration. The assignments for the latter two absorptions are in agreement with the already reported values[32,34] where these weak absorptions at 986-960 cm^{-1} and at 925-900 cm^{-1} (both bands often split) have been attributed to C-H out-of-plane deformation modes.

The 750-670 region:- There are two very strong bands centred around 730 and 700 cm^{-1}. In a number of cases, splitting of one or other of these bands is observed and this together with smaller differences in the frequencies, intensity and shape of the absorption peaks could be used for distinguishing between different phenyltin derivatives. According to Sharp and Sheppard[40] these vibrations are C-H out-of-plane deformation modes. These authors have observed significant shifts (to ca 790 cm^{-1}, 704cm^{-1}) in the spectra of triphenyl-carbonium ion compounds. These higher frequency shifts were consistent with the lower availablity of electrons in triphenyl carbonium cations. As there are no such changes to higher frequency in the out-of-plane C-H frequencies in the spectra of any of the phenyltin compounds, it is not likely that Ph_3Sn^+ cations are present or, if present they have a very different electronic structure than in the Ph_3C^+ cations. This conclusion is further supported by Poller[27] and Kriegsmann

and Geissler[30] who have likewise not observed any frequency shifts in these C-H out-of-plane frequencies.

The Band near 615 cm^{-1} (Whiffen's 's' mode) This is a very weak absorption which is only observed in a few compounds. It is a B_1 class in-plane ring deformation mode[31]. The vibration does not involve the substituent to any extent and it is not sensitive to the substituent. The absorption is assigned as Whiffen's 's' band whenever the phenyltin derivatives show absorption in this region.

The 455-437 cm^{-1} region:- (Whiffen's 'y' band). This is a B_2 class 'X-sensitive' vibration. Randle and Whiffen[32] have described this vibration as an out-of-plane deformation mode and the frequency depends upon the mass of the substituent atom with a limiting value of 433 cm^{-1} for an infinite mass. In the present work, this band has been observed over a wider range between 455-437 cm^{-1} in the spectra of all the phenyltin compounds. The band is of very strong intensity and has often been found split.

The 278-260 cm^{-1} range:- (Whiffen's 't' band) . This is a substituent-sensitve vibration of symmetry A_1 and it occurs between 520-266 cm^{-1} in the infrared spectra of halo-benzenes[31]. All the phenyltin compounds show a medium to strong intensity band in the region 280-260 cm^{-1}. The absorption is usually broad or diffuse in shape. The band has been found to be quite useful in identifying the Ph-X linkage as it involves appreciable C-X stretching and the frequency shows remarkable shift to lower frequency region with the increasing mass of

the substituent atom.

In addition to the benzene ring absorptions as discussed above, there are certain weak and broad bands of uncertain origin. Such absorptions are observed in the far infrared region and no assignments are made for these bands.

Infrared spectra of specific compounds.

Spectra of Ph_3SnOH, $(Ph_3Sn)_2O$ and $(n\text{-}Bu_3Sn)_2O$.

Triphenyltin hydroxide shows a very weak absorption at 3610 cm^{-1} (see Table 5) which is assigned to an OH vibration by anology with the assignment of Kriegsmann and Geissler[30] who have observed a medium intensity band at 3620 cm^{-1} in the spectrum of triphenyltin hydroxide. These workers have recorded the same band at 3636 cm^{-1} in carbon disulphide solution and at 3650 cm^{-1} in carbon tetrachloride solution and have assigned it as an OH stretch. Other workers (West and Baney[41]) have observed this band at 3647 cm^{-1} in the spectrum of triphenyltin hydroxide which they have described as a free OH stretching frequency.

Triphenyltin hydroxide shows a strong doublet at 909 and 898 cm^{-1} which is completely absent in bis-(triphenyltin) oxide. These bands appear to be from an O-H deformation frequencies and similar bands are observed by Kriegsmann and Geissler[30].

Bands associated with the Sn-O group. To obtain an approximate value for the Sn-O stretching frequency an estimate of the force constant was made (Poller[27]) using Gordy's rule[42] and the calculations gave a stretching vibration of 570 cm^{-1}. Although this figure must be regarded as an

approximation, it has been found to be in agreement with the range of absorption reported by Brown, Okawara and Rochow[43] who observed the absorption in the 643-580 cm^{-1} region, for methyltin compounds containing the Sn-O-Sn group. However, Vyshenkii and Rudnevskii[44] examined the spectrum of bis-(triethyltin) oxide and assigned the frequency of an intense absorption band at 788cm^{-1} to the asymmetrical Sn-O-Sn stretching vibration in agreement with the work of Kriegsmann and Geissler[30] who observed a strong absorption at 775 cm^{-1} in bis-(triphenyltin) oxide. The symmetric stretching of the Sn-O-Sn group is expected to be infrared inactive in the $R_3Sn-O-SnR_3$ compounds and this absorption has been recorded at 240 cm^{-1} by Raman spectroscopy for bis-(triphenyltin) oxide[30].

In the present work, the spectra of bis-(triphenyltin) oxide and bis-(tri-n-butyltin)oxide show strong intensity bands at 774 cm^{-1} and at 755 cm^{-1} respectively and these bands are assigned to the Sn-O-Sn asymmetric stretch. In the case of analogous simple disiloxanes the asymmetric Si-O-Si stretching frequency has been found to occur in the 1110-1000cm^{-1} range (Smith[45]) and the results were interpreted in terms of $d_{\pi}-p_{\pi}$ bonding being present in organosiloxanes.

The infrared spectra of triphenyltin hydroxide and hexaphenyldistannoxane are quite distinctive and can easily be distinguished from one another by examination of the region below 1000 cm^{-1}. The existence of the characteristic strong intensity peaks at 744 cm^{-1} for hexaphenyldistannoxane and at

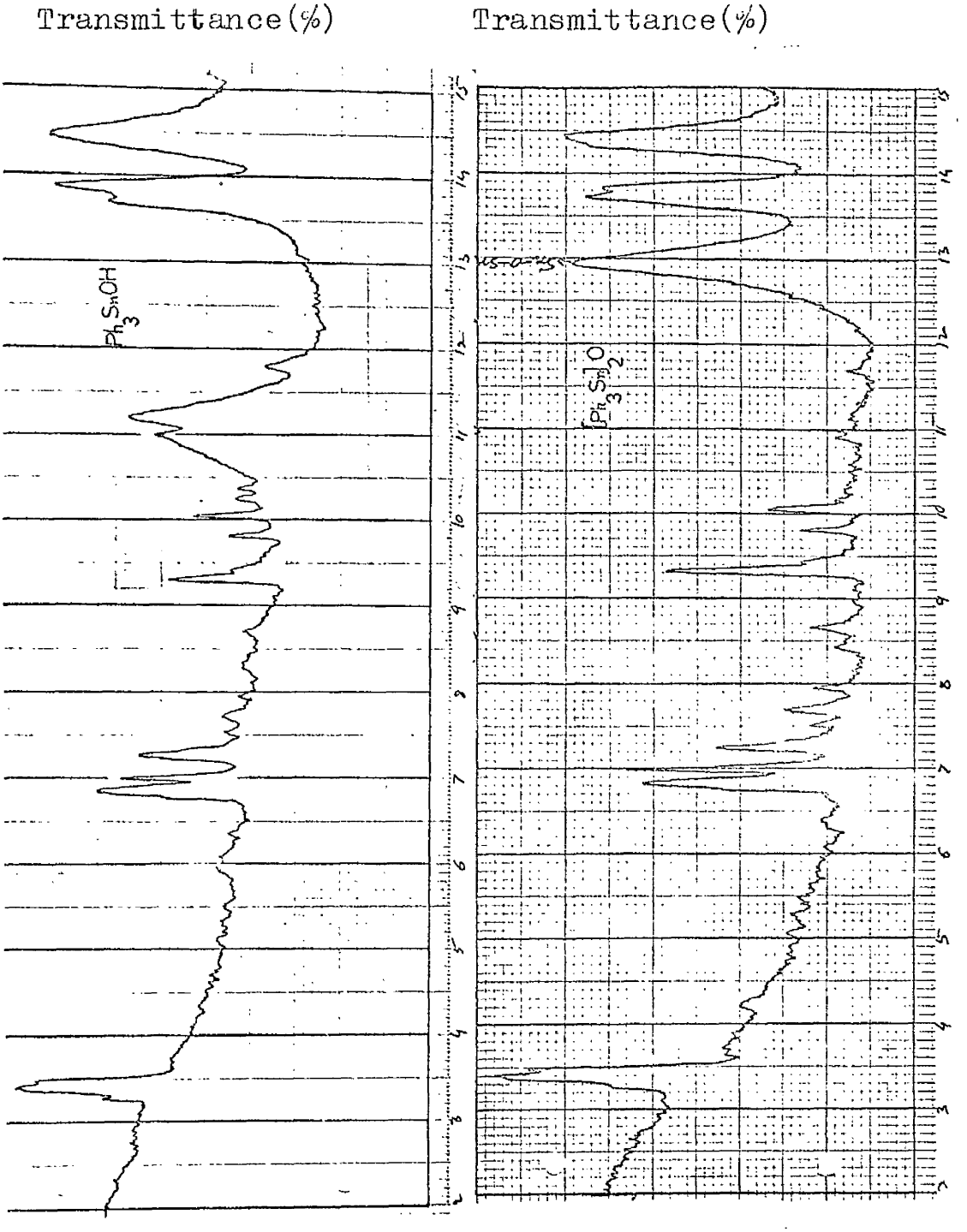


Fig. 4. Infrared spectra of triphenyltin hydroxide and bis-(triphenyltin) oxide in Nujol mulls.

909 and 898 cm^{-1} for triphenyltin hydroxide are experimentally very useful (as shown in Figure 4) for identification purposes since these compounds have similar melting points and are readily interconvertable. In addition to the analytical data the absence of any absorption at 774 cm^{-1} in the spectrum of triphenyltin hydroxide can be used to show that the material is free from the distannoxane. (cf. West, Baney and Powell[50] who concluded that their specimens of the hydroxide contained considerable quantities of hexaphenyldistannoxane).

The halides:- The structure of organotin halides has been discussed by different workers who have each given conflicting statements regarding the nature (covalent or ionic) of these compounds. A large number of organotin compounds which could possibly contain alkyltin cations have been studied by various workers[29,51-55].

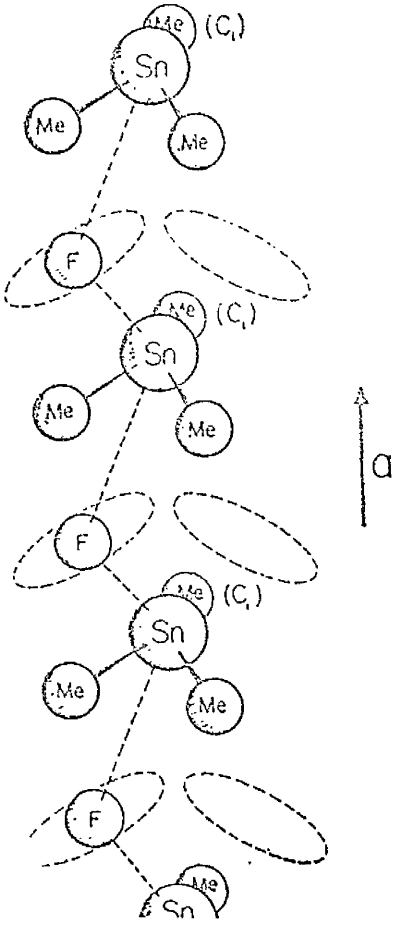
The high melting point and low volatility of trimethyltin fluoride (decomposes $\sim 360^{\circ}$ C without melting) is taken to indicate[55] a salt-like consitution ($Me_3Sn^{+}F^{-}$) for this compound. On the basis of infrared spectroscopic studies (Okawara, Webster and Rochow[51]), trimethyltinfluoride has been considered to be an ionic compound. The infrared and Raman spectra of the trimethyltin halides have been taken to indicate that only the fluoride has an ionic lattice and the other halides i.e. chloride, bromide and iodide were associated through halogen bridging (Kriegsmann and Pischtschan[52]). The tin atoms probably are five co-ordinate.

Recently, the crystal structure of trimethyltin fluoride was studied by Clark, O'Brien and Trotter[53,54] who showed the

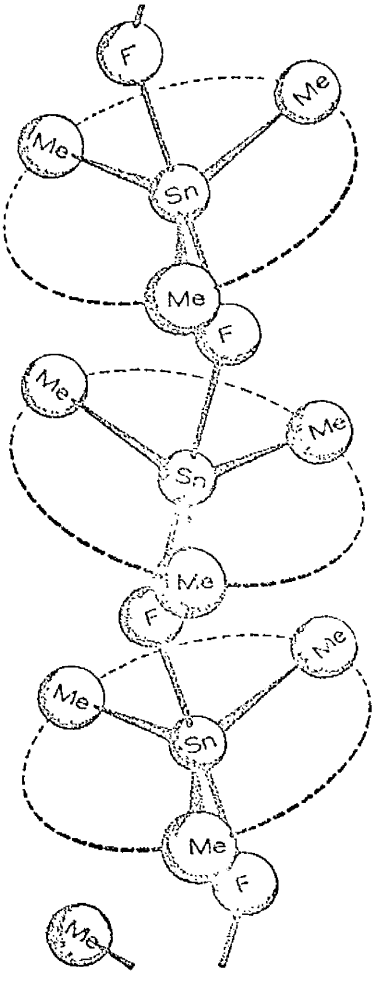
presence of bridging fluorine atoms similar to the structures postulated by Kriegsmann and Pischtschan[52] for other halides. The two possible structures of trimethyltin fluoride are shown in Figure 5. They consist of chains of trimethyltin groups and fluorine atoms along an axis 'a' with only weak Van Der Waals forces between the chains.

Fig. 5 Possible structures of trimethyltin fluoride (Clark, O'Brien and Trotter[53,54]).

I



II



It has been concluded that the structure is not that of a purely ionic solid as the non-linear Sn ---F--- Sn arrangement is a definite indication of covalent interaction. Moreover, each fluorine atom is not equidistant from the two tin atoms so that there is some tendency towards the formation of discrete molecules. The apparent lack of planarity of the trimethyltin group in structure I should have produced an infrared absorption at ca 500 cm^{-1} due to the Sn-C symmetric stretching vibration. Although this had not been previously reported, it was observed by Clark et.al.[53] as a weak intensity band at 515 cm^{-1} in the infrared spectrum of very concentrated Nujol mulls. However, this frequency could just be a forbidden transition of low intensity arising from a planar Me_3Sn group.

In the second structure II, the Me_3Sn groups are planar and are tilted alternatively with respect to the 'a' axis.

Triphenyltin fluoride shows properties which are similar to trimethyltin fluoride. In view of the properties of low solubility and infusability, triphenyltin fluoride was once described as an ionic compound, but Beattie and Gilson[56] have shown that, for trisubstituted tin fluorides, a polymeric structure containing five co-ordinate tin and bridging fluorine atoms may be preferred.

In the present work, the infrared spectrum of triphenyltin fluoride has been found to be quite similar to other phenyltin derivatives. This indicates that the symmetry of

triphenyltin group has not been altered in the fluoride. (cf. infrared changes in the spectra of triphenylmethyl group and triphenylmethyl ion,[40]). Moreover, by analogy with the structure of trimethyltin fluoride (Fig.5), the structure of triphenyltin fluoride is suggested as polymeric with bridging fluorine atoms between the triphenyltin groups. The Sn-F band absorbs at 350 cm^{-1} in the spectrum of triphenyltin fluoride.

On the basis of resemblance with the spectra of other phenyltin derivatives, triphenyltin chloride, bromide and diphenyltindichloride and phenyltin trichloride are concluded as covalent in nature with bridging halogen atoms similar to the structures postulated by Kriegsmann and Pischtschan[52] for the analogous alkyl tin halides.

The tin-halogen group frequencies:- The far infrared spectra (15-50μ) of phenyltin halides and some of the alkyltin fluorides are recorded and the tin-halogen group vibrations, which occur below 400 cm^{-1}, may be assigned as follows. These absorptions are broad and diffuse in shape. From the values quoted in Table 8, it seems that the Sn-F and Sn-Cl absorption frequencies lie very close to each other but in practice the absorption bands are characteristic and can easily be identified as shown in Figures 6-8.

The Sn-F frequency:- The spectrum of triphenyltin fluoride shows a broad band at ca 350 cm^{-1} and all other bands are similar to those of tetraphenyltin (see Figure 6) and are assigned to vibrations of a mono-substituted benzene group

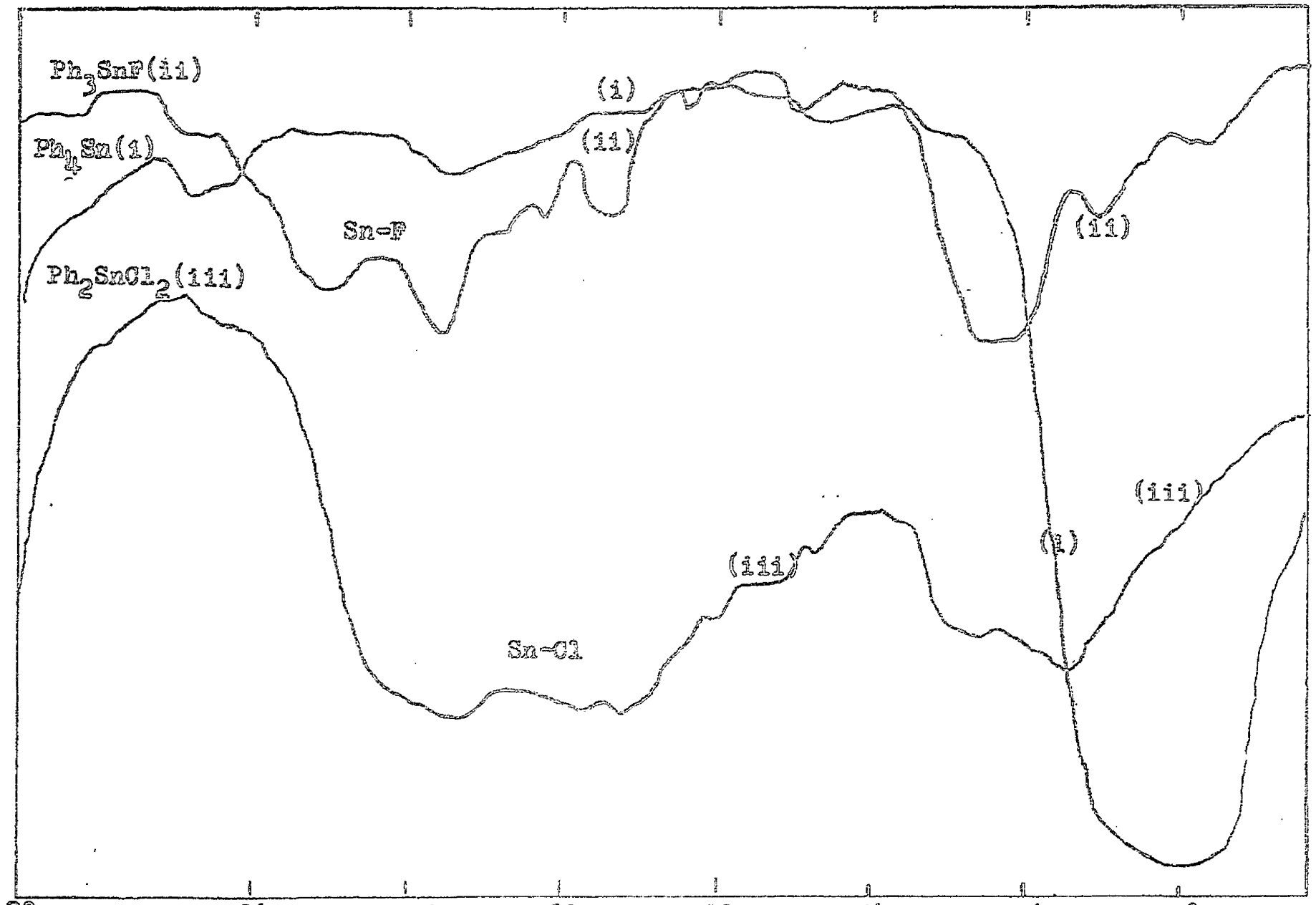


Figure 6 Far infrared spectra of organotin halides.
(i) Tetraphenyltin (ii) Triphenyltin fluoride (iii) Diphenyltin dichloride

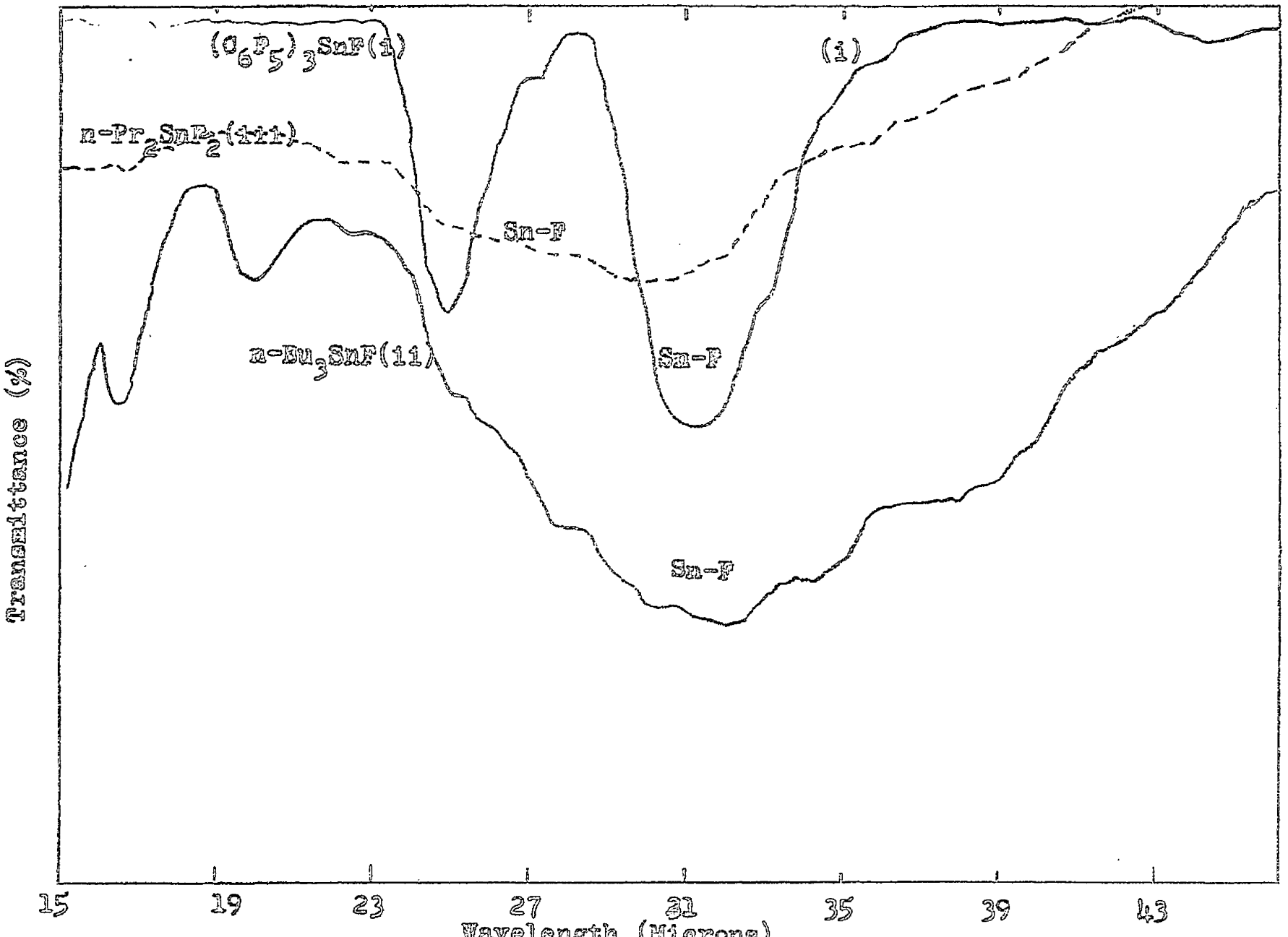


Figure 7. Far infrared spectra of organotin fluorides
(i) Tris-pentafluorophenyltin fluoride (ii) Tri-n-butyltinfluoride
(iii) Di-n-propyltin difluoride

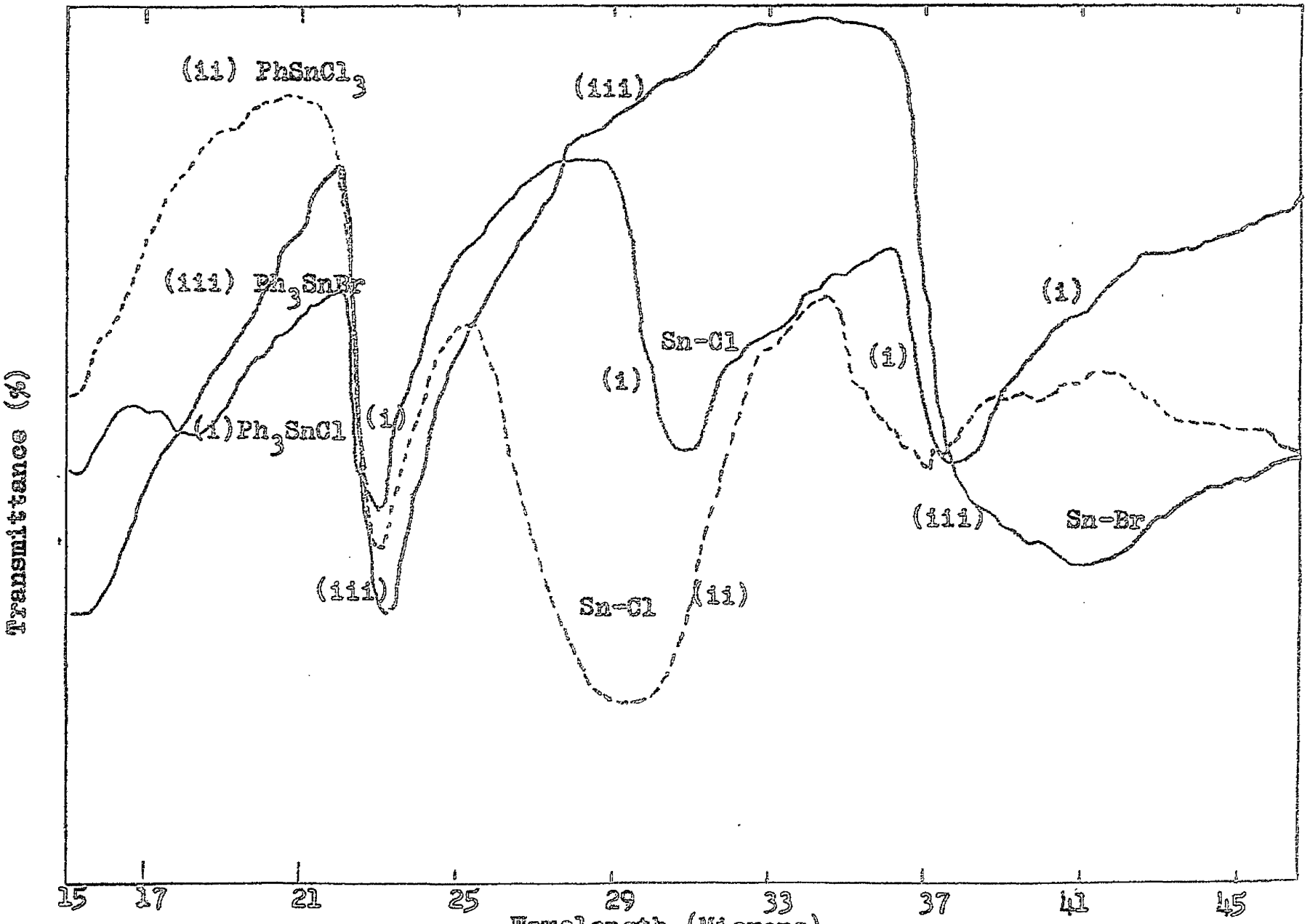


Figure 8 (i) Triphenyltin chloride (ii) Phenyltin trichloride (iii) Triphenyltin bromide.

Compound	tin-halogen frequency (cm^{-1})
Ph_3SnF	350
$(C_6F_5)_3SnF$	328
$n\text{-}Bu_3SnF$	330
$n\text{-}Pr_2SnF_2$	330
Ph_3SnCl	~ 330
Ph_2SnCl_2	~ 370-312
$PhSnCl_3$	340
Ph_3SnBr	267

(see table 4). It is considered that this extra absorption band at 350 cm^{-1} is from a Sn-F stretching mode. Similar bands are found in the spectra of tris-(pentafluorophenyl)tin fluoride (328 cm^{-1}), tris-(n-butyl)tin fluoride (330 cm^{-1}) and di-(n-propyl)tin difluoride (330 cm^{-1}). In the spectra of all these compounds (fluorides) there is no other assignment that can be made; except that these absorption bands are Sn-F vibrations. It is not possible to make a direct comparison with the frequencies of Sn-F bonds in other tin compounds, since there is no certainty that the same co-ordination arrangement about the tin atom is present in the compounds described in the present work. Kriegsmann and Kessler[57] report

the following values of Sn-F frequencies.

Table 9

	Sn-F frequencies (cm^{-1})	
	ν_{as}	ν_s
SnF_6^{2-}	564	-
SnF_3^-	478	552
SnF_2	457	552

Sn-Cl valence vibrations (νSn-Cl) have been reported for a variety of tin compounds. The literature frequencies are given below in Table 10. It can be seen that the Sn-Cl frequencies, for the phenyltin derivatives, examined in the present work, are in fair agreement with those in the literature. The absorption frequencies of phenyltin chlorides lie close to those of trimethyltin chloride and stannic chloride, suggesting a similar co-ordinate arrangement about the tin atom, in phenyltin chlorides. The assignment for the Sn-Br vibration in Ph_3SnBr is made on the basis that the compound shows a very strong intensity band at ca 265 cm^{-1} and the other phenyltin halides do not absorb in this region.

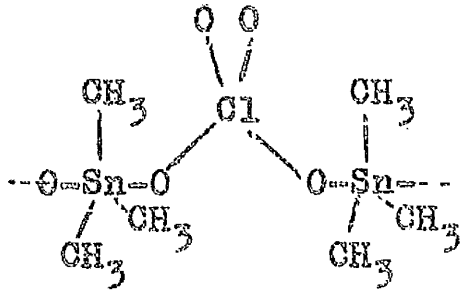
The perchlorates.- Trimethyltin perchlorate has been prepared in an anhydrous form by Clark and O'Brien[55]. The perchlorate sublimed at low temperature and melted in a sealed tube at 125-127° C. These physical properties are not consistent with an ionic structure for this compound. The infrared spectrum of trimethyltin perchlorate has extensively

Table 10 Sn-Cl absorption frequencies

Compound	Sn-Cl frequency (cm^{-1})	Reference
$SnCl_4$	368 366	58 59
$SnCl_6^{2-}$	314	60
$(NO)_2SnCl_6$	310	61
Crystal violet $SnCl_4$ complex	317	62
Me_3SnCl	331 336	52 14
Ph_3SnCl	328 330	30 present work
Ph_2SnCl_2	~ 370-312b	present work
$PhSnCl_3$	340	present work

been investigated by Clark and O'Brien[55]. The infrared absorption for the perchlorate group was found to be in favour of a covalent structure as postulated by Ross[63] and Hathaway and Underhill[64]. Thus on the infrared evidence, it

has been concluded that trimethyltin perchlorate is composed of planar trimethyltin groups bridged by partially covalent perchlorate groups to form chains as shown in Structure (III)



III

In the present work, it was proposed that if there is any possibility of obtaining an o'nium salt, that could contain a triphenyltin cation, it would contain an anionic group derived from a very strong acid. Thus in order to gain further information on the structure of triorganotin compounds, triphenyltin perchlorate was obtained by reacting triphenyltin chloride with anhydrous silver perchlorate in ether under completely unhydrous conditions. The infrared spectrum is the same as observed for other phenyltin derivatives and is definitely not in favour of a new Ph_3Sn^+ entity. The perchlorate group absorbs in the 910-1200 cm^{-1} region. The peaks are split, are of high intensity and are similar to the bands reported for trimethyltin perchlorate (Clark and O'Brien [55]) being explicable by the perchlorate group acting as a bidentate bridge of symmetry C_{2v}. By analogy with the suggested structure of trimethyltin perchlorate, it is suggested that the structure of triphenyltin perchlorate

involves planar triphenyltin groups bridged by perchlorate groups and that the tin atom is penta co-ordinate, most likely with a trigonal bipyramidal structure as in trimethyltin fluoride (Clark, O'Brien and Trotter[53,54]) and in $Me_3SnClpy$ (Beattie, McQuillan and Hulme[14]).

The present picture of the structure of triphenyltin perchlorate is in agreement with Clark's most recent private communication. He has also prepared this compound and his infrared studies have been found to support the same conclusion as derived above.

The fluoroborates:- Trimethyltin tetrafluoroborate has recently been prepared (Hathaway and Webster[66]) by the reaction of trimethyltin chloride with silver tetrafluoroborate in methyl cyanide solution. This compound has been reported (Burg and Spielmann[65]) as a white amorphous hygroscopic solid and it has melting point 80°C. Hathaway and Webster[66] have interpreted, the infrared spectrum of trimethyltin tetrafluoroborate, by assuming a covalent structure with bridging through two of the fluorine atoms of the tetrafluoroborate group. In the previous literature[67] the tetrafluoroborate ion has generally been considered to be a non-complexing anion as the required co-ordination, for complexing, of two for the fluorine atom is rare.

The BF_4^- ion has Td symmetry and there are nine vibrational degrees of freedom distributed between four normal modes of

vibration of which only two (ν_3 and ν_4) are infrared active (Greenwood[68]). In the infrared spectrum of trimethyltin tetrafluoroborate, the ν_3 vibration has been found split into three componenets, (Hathaway and Underhill[64]) and this splitting is taken to indicate a lowering of symmetry of the anion because two of the fluorine atoms are acting as bridging between the two organotin groups. On this evidence, the structure of trimethyltin tetrafluoroborate has been formulated as a chain structure with tetrafluoroborate groups forming bridges between separate trimethyltin groups.

Triphenyltin tetrafluoroborate has not been reported previously. The first preparation of this compound was attempted (Sharp and Winfield[69]) by reacting boron trifluoride with tetraphenyltin at 140°C by analogy with the tetramethyltin reaction (Burg and Spielman[65]). A product that decomposed at 90°C, on attempted sublimation, was formulated as triphenyltin fluoroborate. In the present work Ph_3SnBF_4 was prepared by reacting triphenyltin chloride with an equivalent quantity of silver fluoroborate in ethereal or benzene solution. Silver chloride precipitated out and the removal of the solvent gave an oily or gummy material. The compound showed a very strong interaction with the solvent and it was impossible to remove final traces of solvent from the reaction product. Because of the extremely bygroscopic nature of

Ph_3SnBF_4, it has not proven possible to obtain a crystalline sample for analysis.

The infrared spectrum of Ph_3SnBF_4 shows bands characteristic of a monosubstituted benzene group (similar to other phenyltin derivatives) and a broad absorption split into two bands at 1072 and 1020 cm^{-1} in the B-F absorption region. The splitting of the ν_3 frequency into two or three componenets indicates lowering of symmetry of the tetrafluoroborate ion. The lowering of symmetry most probably arises from a strong interaction of fluorine atoms with triphenyltin groups. Thus by analogy with the suggested structure of trimethyltin fluoroborate (Hathaway and Webster[66]), it seems most likely that triphenyltin fluoroborate has a covalent structure with bridging tetrafluoroborate groups, and the tin atom is present in a five co-ordinate state.

Structure of some other related organotin compounds:-

On the basis of infrared spectrum, trimethyltin nitrate has been postulated (Clark and O'Brien[55]) to contain unidentate nitrato group linked to a non-planar trimethyltin group. Similarly, more recent work (Addison, Simpson and Walker[70]) on the infrared spectrum of dimethyltin dinitrate, has shown that the compound contains unidentate nitrate groups ($-ONO_2$) attached covalently to the alkyltin group.

Even the compounds containing the strongest electronegative anions (e.g. MF_6^- type) show strong interaction with the organo-tin groups. The infrared spectra of trimethyltin hexafluoroarsenate and hexafluoroantimonate (Clark and O'Brien[29]) show splitting of the hexafluoroarsenate and hexafluoroantimonate group absorptions whereas the free ions should show (Peacock and Sharp[71]) only a single absorption band in the regions studied. This splitting indicated a lowering of symmetry of the hexafluoro anions and has been taken to indicate that these derivatives are polymeric in structure, similar to the organotin perchlorate and fluoroborate as described in the present work.

It has not been possible to obtain any R_3SnX compound in which there existed a free R_3Sn^+ ion. In all cases the tin atom is essentially five co-ordinate.

Miscellaneous Topics:- During the course of the work a number of reactions were attempted with phenyltin derivatives. These are not conveniently classified eleswhere and are dealt with here.

Reaction of triphenyltin fluoride with boron trifluoride

Triphenyltin fluoride was reacted with boron trifluoride in a bomb, liquid sulphur dioxide being used as a solvent. It was expected that a reaction would occur and the $\emptyset_3SnBF_4$ would be the reaction product. The infrared spectrum of the

resultant product was found to be identical with the spectrum of triphenyltin fluoride and there was no absorption in the B-F region. In another attempt triphenyltin fluoride was reacted with boron trifluoride in benzene solution but the reaction product isolated was again characterised as Ph_3SnF. From these experiments it is concluded that triphenyltin fluoride does not react with boron trifluoride. This lack of reactivity of triphenyltin fluoride is attributed to the high lattic energy of the compound. This unreactivity of organotin fluorides has also been reported by Clark[94] who has attempted the preparation of R_3SnPF_6 by reacting R_3SnX compounds with PF_5. The products isolated were identified as R_3SnF and not as hexafluorophosphates.

Reaction of triphenyltin fluoride with $CF_3C{\equiv}CCF_3$

The unreactive nature of triphenyltin fluoride was further substantiated by the attempted reaction with hexafluorobut-2-yne, when a simple addition product $CF_3(Ph_3Sn)C{=}CFCF_3$ or $CF_3(Ph_3Sn)CF{-}CF(PH_3Sn)CF_3$ was expected. Triphenyltin fluoride was recovered unchanged from the reaction mixture. Such addition reactions are shown by other organotin derivatives. For instance, the addition reactions of organotin hydrides to olefines and acetylenes have been studied by Kerk and Noltes[72].

(i) $Ph_3SnH + HC{\equiv}CR' \longrightarrow Ph_3SnCH{=}CHR'$

$Ph_3SnCH{=}CHR' + Ph_3SnH \longrightarrow Ph_3SnCH_2{-}CHR'SnPh_3$

(ii) $(C_4H_9)_2SnH_2 + 2CF_2{=}CF_2 \longrightarrow (C_4H_9)_2Sn(CF_2{-}CF_2H)_2$

It has been suggested that organotin radicals or cations may be present as reactive intermediates in these reactions.

The Acetates:- The preparation of $Ph_3SnOOCH_3$, $Ph_3SnOOCCF_3$ and $Ph_2Sn(OOCCF_3)_2$ has been carried out by reacting the corresponding organotin chlorides or bromides with equivalent proportions of silver acetate or trifluoroacetate in anhydrous ether, while shaking the reaction mixtures overnight. This is a new procedure for preparing these derivatives. $Ph_3SnOOCCF_3$ and $Ph_2Sn(OOCCF_3)_2$ are new compounds. The preparation of these phenyltin acetates has also been attempted by the procedure described by Anderson[73] who reported dealkylation of tetralkyltins by refluxing with metallic acetates or trifluoroacetates. Triphenyltin acetate was prepared by refluxing equivalent proportions of tetraphenyltin and silver acetate in toluene. Attempts were made to prepare $Ph_2Sn(OOCCH_3)_2$ by using two equivalents of silver acetate but the reaction product was found to be $Ph_3Sn(OOCCH_3)$. Even the use of an excess of silver acetate yielded only the mono-acetate.

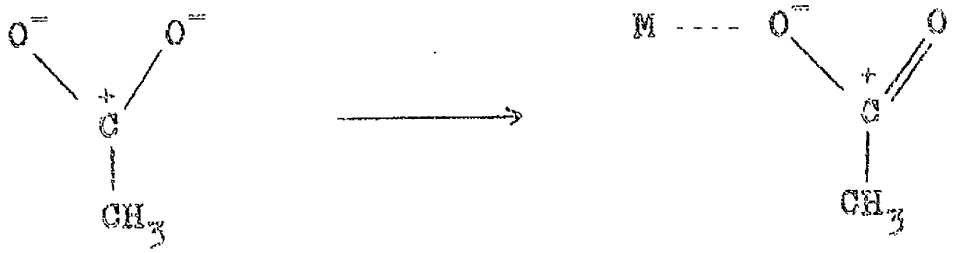
The cleavage of the Sn-C bond by electrophillic reagents has been discussed by many authors[73-81]. In the present work, it seems that the cleavage of the C_{aryl}—Sn bond depends upon the electronegativity of the attacking acid anion as the attempts to prepare $Ph_2Sn(OOCCH_3)_2$ from tetraphenyltin gave only a mono-acetate whereas $Ph_2Sn(OOCCF_3)_2$ was obtained without any difficulty. It could, however, also be due to the different solubility of diphenyltin diacetate or the different effect of the acetate group when one acetate group is substituted to form a mono-acetate.

From infrared studies (Freeman[82]; Okawara, Webster and Rochow[51]; Okawara and Sato[83]) of methyltin esters, it was inferred that the carboxylate group was ionic and the dimethyltin and trimethyltin groups existed as cations. Similarly from a consideration of infrared spectra (Olah[84]) of the compounds. $Me_3SiOOCCH_3$, $Me_2Si(OOCCH_3)_2$, $MeSi(OOCCH_3)_3$, $Si(OOCCH_3)_4$, $Me_3SnOOCCH_3$, $Me_3SnOOCH$, Me_3Sn chloroacetates, $Me_3SnOOCC_2H_5$, Me_3Sn halides, $Me_2Sn(OOCCH_3)_2$, $Me_2Sn(OOCH)_2$, Me_2Sn dihalides, MeSn trihalides it has been concluded that the silicon derivatives are covalent but that the tin compounds contain methyltin cations. However, Beattie and Gilson[85] and Van Der Kerk and co-workers[86,87] have proposed that the spectroscopic evidence on acetate groupings may equally well be

interpreted in terms of either bridging or chelated acetate groups, or simple acetate ions. If the former is the true picture, $Me_3SnOOCH_3$ would contain planar Me_3Sn groups linked by bridging acetate groups as described by Van Der Kerk, Luijten and Janssen [86]. The tin atom would be penta-co-ordinate as postulated for other organotin compounds.

Triphenyltin acetate and triphenyltin trifluoroacetate have relatively low melting points and are soluble in ether and other organic solvents. These properties favour covalent rather than ionic structures for these compounds, and the infrared spectra are in agreement with this as discussed below.

The significance of the degree of separation of the two C-O stretching modes (ν_1 sym. and ν_2 asym.) in phenyl carboxylates and in other related compounds has been discussed by various workers[27,51,91-93]. According to Nakamoto, Fujita, Tanaka and Kobayashi[92] the separation of the two C-O stretching frequencies has been found to increase when the metal-oxygen bond becomes stronger and the two C-O bonds of the acetate ion become uneven as shown below.



On the other hand Okawara, Webster and Rochow[51] have associated the band separation with the strength of the carboxylic acid. A plot of the C-O band separations taken from Okawara's paper against p^K values for the carboxylic acids gave a straight line for all the compounds except trimethyltin formate (Poller[27])

We have now studied (Table 11) the C-O band separations $(\nu_2-\nu_1)$ in triphenyltin acetate and the phenyltin trifluoro-acetates. The absorptions for triphenylacetate are similar to those obtained by Okawara et.al [51] for a number of alkyltin acetates. It is clear that the differences between the asymmetric and symmetric C-O stretching modes for alkyltin acetates and halogenated acetates are of the same order as those between the corresponding sodium salts of the carboxylic acids The band separation $(\nu_2-\nu_1)$ increases with the increasing acidic strength of the carboxylate group.

Before the completion of the present work Clark[94], Janssen, Luijten, and Van Der Kerk[90] and Cummins and Dunn[92] reported infrared studies on some other trialkyltin acetates, the conclusions are similar to those reported here.

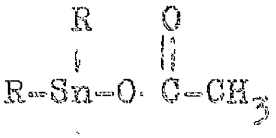
The spectral changes with changes of temperature[91] and with increasing concentration of organotin acetates[94] have been taken to indicate that the acetates are present in monomeric ester-like covalent form in molten state and in dilute solutions. In the solid state and in concentrated

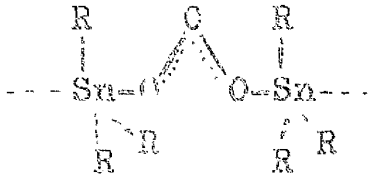
Table 11 — C=O Stretching frequencies in cm^{-1}

Compound	Sym. stretch ν_1	Asym. stretch ν_2	Band Separation $\nu_2-\nu_1$	Reference
$(CH_3)_3SnOOCCH_3$	1433	1574	141	51
$n\text{-}Bu_3SnOOCCH_3$	1417	1570	153	91
$NaOOCCH_3$	1440	1576	136	91
$Ph_3SnOOCCH_3$	1425 1430	1530 1534	105 104	27 p
$Ph_3SnOOCC_6H_5$	1335	1620	285	27
$(CH_3)_3SnOOCCCl_3$	1352	1656	304	51
$n\text{-}Bu_3SnOOCCCl_3$	1340	1646	306	91
$NaOOCCCl_3$	1352	1672	320	91
$AgOOCCF_3$	x	1640		p
$Ph_3SnOOCCF_3$	x	1656sh,1645		p
$Ph_2SnOOCCF_3$	x	1670sh,1645		p

p present work x absorptions masked by Nujol or other peaks.

solutions (>30%) the acetates exist as chelated covalent compounds with symmetrical acetate groups bridging between two organotin groups. Thus from the available evidence, it is concluded that alkyl and aryl tin carboxylates or halogenated acetates are predominately covalent compounds and their structures, as deduced from infrared spectroscopy, are shown below.

(a)  IV

(b)  V

R = alkyl or aryl.

(a) Monomeric covalent structure of triorganotin acetates present in dilute solution or in the molten state.

(b) Polymeric chelated covalent structure of organotin carboxylates in concentrated solution or in solid state.

The C-F vibrations:- The C-F frequency assignments for the phenyltin trifluoroacetates are made after Randle and Whiffen[95] who have studied the characteristic C-F stretching vibrations of the CF_3 group. They have assigned these modes near 1180cm^{-1} and near 1140 cm^{-1}.

In the present work, the corresponding C-F assignments for the trifluoroacetates are shown below:

Table 12

Compound	C-F Vibrations cm^{-1}		
$AgOOCCF_3$	1198vs,	1150s, 855s, 800s, 735s	
$Ph_3SnOOCCF_3$	1195sh, 1190vs, 1163s,	1149s,	843m, 801w, 792m
$Ph_2Sn(OOCCF_3)_2$	1198vs,	1149s,	847m, 805m, 787m

These assignments are in fair agreement with those values as reported by Randle and Whiffen[95]

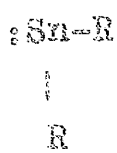
Infrared spectrum of tetrakis-pentafluorophenyltin $(C_6F_5)_4Sn$

According to Birchall and Haszeldine[97] the C-F vibrations in perfluorobenzene derivatives, occur near 1000cm^{-1}. In the present work, the infrared spectrum of $(C_6F_5)_4Sn$ shows absorption bands at 1087, 1076 and 962 cm^{-1} which are assigned to C-F stretching modes by comparison with the values reported by Birchall and Haszaldine[97] for other perfluorobenzene derivatives. Similarly the absorption bands at 1513 and 1471cm^{-1} are assigned as ring vibrations by analogy with the work already reported[97].

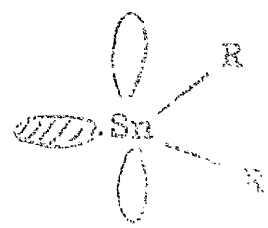
The Structure of diphenyltin:- The compounds of Sn II are usually colourless but diphenyltin is reported (Kuivila et.al [98]) with various colours, to be monomeric or polymeric, to be highly air sensitive or air stable and to have a range of

solubilities. The molecular weights have been found to be variable. Magnetic susceptibility measurements on this compound have shown (Krause and Pohland[99]) that diphenyltin is not present as a radical and the low dipole moment of the monomeric and polymeric forms indicate (Jensen and Clauson-Kaas[100]) that the compound is not polar.

The two covalent state of Group IVA elements has been described[101,102] as arising from s^2p^2, (^3P in the Russel-Saunders notation), ground state of the atom structure VI or VII and

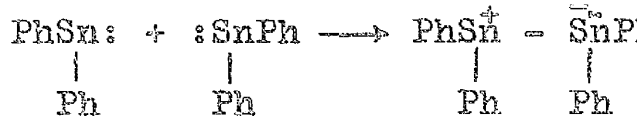


VI



VII

the expected bond angle would be approximately 90° for for s^2p^2 bonding. Electron diffraction measurements (Lister and Sutton[103]) on SnII chloride in the vapour phase have shown that the molecule is angular. As the central tin atom in structures VI or VII has only six valency electrons, polymerisation is expected to occur in order to obtain a stable octet configuration. Ingham, Sanders, Rosenberg and Gilman[104] have suggested the polymerisation of diphenyltin as follows:-



Such polymerisation will make the tin atom four co-ordinate and the structure is in agreement with the infrared data reported by Neumann and Konig[105].

In the present work the infrared spectrum of diphenyltin was compared with those of the Sn(IV) compounds and was found to be almost identical with the spectrum of tetraphenyltin. From this evidence it is suggested that diphenyltin and tetraphenyltin have a very similar arrangement for the co-ordination about the tin atom. A structure for diphenyltin in which a phenyl group is acting as a bridge between tin atoms would show a different infrared spectrum and hence this structure can be ruled out.

Dissociation of compounds of the type Ph_3M-MPh_3

An investigation was made of the dissociation of derivatives of the type Ph_3M-MPh_3 (where M=Sn, Pb). The data on the dissociation of the compounds are scattered throughout the literature and far from complete. The extent to which these phenyl derivatives dissociate has been the subject of several conflicting statements.

It has long been known that hexaphenylethane dissociates homolytically in solution to form triphenylmethyl radicals (Gomberg[112]). Subsequently, it was found that a triphenylmethyl radical can either lose or gain one electron to give

a charged triphenylmethylcation $(Ph_3C)^+$ or an anion $(Ph_3C:)^-$. In hexaphenylethane the steric repulsion energy of the two halves is estimated to be about 36 kcal/mole and the enthalpy of dissociation is about 16.5 kcal/mole (Pauling[96a]). This explains the easy dissociation of hexaphenylethene. However, it has been pointed out (40,96b,113) that there would be steric hinderance in the triphenylmethyl cation or radical and that the resulting strain in triphenylmethyl entity could be relieved by rotation of the phenyl groups.

The abnormal stability of the triphenyl radicals or ions has been attributed (Pauling and Wheland[113]) to resonance, so that the odd unpaired electron or charge becomes associated with a relatively large number of canonical forms.

The hexaphenyldisilanes do not appear to be dissociated in solution and no free radicals can be detected (Sidgwick[115]; Petro and Smyth[116]). It is, however, postulated that Ph_3Si radicals are present as reactive intermediates in radical induced reactions of Ph_3SiH. From ebullioscopic measurements, Morgan and Drew[117] have concluded that hexaphenyldigermane does not show a recognisable tendency to dissociation in dilute benzene solution. Hexaphenylditin is a colourless substance. Böeseken and Rutgers[118] have carried out molecular weight determinations on solutions of several distannanes and they have shown that these compounds in concentrations of a few per

cent have normal molecular weights, whereas in concentrations of a few tenths of a per cent, they appeared almost completely dissociated. For example hexaphenylditin showed 50% dissociation in 0.87% benzene solution at 5°C. However, these observations are not in agreement with the magnetic susceptibility studies on hexaphenylditin by Morris, Byerly and Selwood[119] who have ruled out the presence of free radicals. The only other possiblity for dissociation of such compounds is the heterolytic dissociation.

$$Ph_3Sn - SnPh_3 \rightleftharpoons Ph_3Sn^+ + Ph_3Sn^-:$$

This has been questioned (Coates[120]) on the basis that Ph_3Sn^+ cation would be expected to be coloured by analogy with the colour of Ph_3C^+ cation, but this reasoning does not seem to be valid as the orbitals which would be used in forming the Ph_3Sn^+ cation would be very different from those used in forming the Ph_3C^+ cation. The solvation of the cation should also cause a loss of colour. It may be suggested that hexaphenylditin derivatives are solvated by a charge transfer mechanism between solvent benzene and the phenyl groups. Such solvation would explain the anomolous molecular weights of these compounds.

Hexaphenyldilead is yellowish in colour and it shows changes in colour with change in temperature in benzene or nitromethane solution. The cryoscopic measurements on this compound in

benzene solution showed the same degree of dissociation as in the case of the corresponding distannanes (Krause and Reiszaus [121]). However, the molecular weight determinations (Malatesta [124]) have shown that hexaphenyldilead did not dissociate in melting naphthalene. Similarly from magnetic measurements on hexaphenyldilead(112,123), it was concluded that there was no recognisable dissocation of this compound.

In view of this contradictory situation, it was proposed to examine the conductitities of hexaphenylditin and hexaphenyldilead. The results of conductivity measurements are shown in the following Table. The measurements were carried out in nitromethane solution.

The results of the conductivity measurements show that hexaphenylditin and diphenyldilead do not dissociate heterolytically and the extent of their dissociation is not detectable and is certainly less than 1%.

It seems that in considering the dissociation of R_3M-MR_3 compounds, resonance, steric hinderance and the metal-metal bond strength all play an important part. The easy dissociation of hexaphenylethane is probably due to the first two of the above factors and it seems certain that the distannanes and diplumbanes do not dissociate because of the stronger metal-metal bonds.

Table 13

Solution	Conductivity in milli 'mhos' at different temperatures		
.0156M	18° C	30° C	40° C
Hexphenylditin		.000491	.000516
.01M			
Hexaphenyldilead	.00033	.00034	.00036
.016M			
Sodium iodide		.035	

Note:- Hexaphenyldilead did not give a clear solution.

Experimental

Preparation of silver tetrafluoroborate:-

This compound was prepared using the following two methods:-

(i) By reacting dry silver borate with bromine trifluoride in a silica tube (Sharpe[125]).

(ii) Silver fluoride was prepared by reacting silver carbonate with aqueous hydrofluoric acid in a platinum dish (Anderson, Bak and Hillbert[127]). Then silver tetrafluoroborate was obtained by reacting silver fluoride with boron trifluoride using sulphur dioxide as the solvent. (Russell and Sharp[126]).

From the two methods used for the preparation of silver fluoroborate, the first method is convenient when smaller quantities of the material are required and the second procedure is useful for obtaining larger quantities of silver tetrafluoroborate.

Purification of silver perchlorate:- The compound was recrystallised from anhydrous ether. The recrystallised compound was dried *in vacuo* and stored over phosphorous pentoxide in a desiccator.

Preparation of silver trifluoroacetate:- Silver carbonate was dissolved in trifluoroacetic acid, the solution filtered off and silver trifluoroacetate was obtained by evaporating the filtrate. The compound was recrystallised from anhydrous ether. The final product was dried *in vacuo* and kept over

phosphorous pentoxide in a desiccator. The absence of moisture was confirmed by its infrared spectrum.

Preparation of organo-tin compounds:- All the known compounds were prepared by standard procedures. The reactions were carried out under strictly anhydrous conditions wherever necessary. The compounds were characterised by carbon and hydrogen analysis and the melting points found were in agreement with the previously reported values. The details of analysis are given in Table 14.

Tetraphenyltin (Ph_4Sn) was of the commercial grade (from Pure Chemicals Ltd.) and was recrystallied from benzene. This compound was used as a starting material for the preparation of most of the other aryltin derivatives.

Triphenyltin hydroxide (Ph_3SnOH) was prepared according to the method of Kraus and Pohland[110].

Bis-(triphenyltin) oxide ($Ph_3Sn-O-SnPh_3$

Triphenyltinhydroxide was heated at 90-100° C for four hours in vacuo. The product was recrystallised from acetonitrile. The infrared spectrum of the product did not show a strong absorption at 909m, 898s cm^{-1} which is characteristic for triphenyltin hydroxide. The disappearence of this absorption and appearence of an other strong intensity band at 774 cm^{-1} (Sn-O-Sn) confirmed the complete convertion of the hydroxide into the oxide.

Attempts were also made to prepare bis-(triphenyltin) oxide by the method described by Kushlefsky, Simmons and

Ross[128] but the method gave only tetraphenyltin.

Bis-(tri-n-butyltin) oxide $(Bu_3Sn)_2O$ was prepared by shaking an ethereal solution of tri-n-butyltin chloride with aqueous potassium hydroxide (Luijten and Van Der Kerk[129]). After evaporating off the ether, an oily liquid was obtained which was heated at 80-90° C for about eight hours *in vacuo* to give bis-(tri-n-butyltin) oxide.

Triphenyltin fluoride (Ph_3SnF).

As compared with other phenyltin halides, the fluoride has a very low solubility (Coates[120]). It was prepared by adding aqueous hydrofluoric acid to a hot alcoholic solution of triphenyltin chloride in a polythene container. The fluoride precipitated out. The precipitate was washed with alcohol and dried under vacuum.

Triphenyltin chloride (Ph_3SnCl)

(Kozeschkow, Nadj, and Alexandrow[130]).

A mixture of .445 mole tetraphenyltin and .148 mole stannic chloride was heated at 205-215° C in an oil bath for three hours and subsequently at 180-190° C for three hours. The reaction product was recrystallised from anhydrous ether.

Triphenyltin tetrafluoroborate (Ph_3SnBF_4).

Triphenyltin chloride was reacted with an equivalent proportion of silver fluoroborate in ethereal or benzene solution. On mixing the two solutions, silver chloride was precipitated and was filtered off in a dry box. The removal of the solvent gave an oily or gummy material which showed

absorptions in the B-F region. The infrared spectrum also showed characteristic absorptions for mono-substituted phenyl groups as do all phenyltin derivatives. Thus it is certain that the product is Ph_3SnBF_4, but it has not been possible to obtain a crystalline sample for analysis as the product showed a very strong interaction with the solvent or moisture and it was impossible to remove final traces of the solvent from this compound.

Attempted preparation of triphenyltin fluoroborate by reacting triphenyltin fluoride with boron trifluoride.

This reaction was carried out in a stainless steel bomb (from Baskerville and Lindsay Ltd.) of 25 ml. capacity. Triphenyltin fluoride (about 1 gm.) was placed in the bomb which was evacuated and about 3-4 ml. of sulphur dioxide was condensed into the bomb, followed by an excess of boron trifluoride. The charging of sulphur dioxide and boron trifluoride was carried out on a vacuum line. The bomb was rocked overnight at room temperature. The excess sulphur dioxide and boron trifluoride were allowed to escape and the product left in the bomb was pumped on for about two hours, the bomb was opened in the dry box and the infrared spectrum of the solid product was found to be identical with the starting material.

In another attempt triphenyltin fluoride was reacted with boron trifluoride in benzene, but the attempt to prepare triphenyltin tetrafluoroborate was again unsuccessful and triphenyltin fluoride was isolated.

Reaction of triphenyltin fluoride with hexafluorobut-2-yne

Hexafluorobut-2-yne was prepared by reacting 1,1,1,4,4,4-hexafluoro-2,2,3,3-tetrachlorobutane with zinc dust in acetic anhydride (Krespan, Harder and Drysdale[140]).

About one gram of triphenyltin fluoride was reacted with an excess of hexafluorobut-2-yne in a stainless steel bomb. The bomb was heated at about 100°C for 12 hours. After pumping out the unreacted gas, the reaction product was handled in a dry box. The infrared spectrum did not show absorption in the C-F region and the spectrum was identical with the infrared spectrum of triphenyltin fluoride.

Triphenyltin perchlorate (Ph_3SnClO_4) was prepared by the same procedure as used for Ph_3SnBF_4. The product was gummy and the infrared spectrum showed the characteristic absorption for the perchlorate group as well as for the monosubstituted phenyl groups. This evidence indicates the formation of this compound but analytical results could not be obtained as the attempts to prepare a crystalline sample were not successful.

Diphenyltin dichloride (Ph_2SnCl_2) was prepared according to the method of Kozeschkow[131]. Equivalent quantities of tetraphenyltin and stannic chloride were heated at 220°C for 1½ hours. The reaction product was recrystallised from light petroleum.

Phenyltin trichloride ($PhSnCl_3$) was prepared by reacting tetraphenyltin with stannic chloride according to the method of Kozeschkow[131]. 0.05 mole of tetraphenyltin and 0.15 mole of stannic chloride were heated at 210-220°C for two hours. The reaction was carried out under completely anhydrous conditions. The reaction product was an oily liquid. Phenyltin trichloride was fractionated under vacuum. The infrared spectrum confirmed the absence of moisture and of hydrolysis products.

Found b.p. 140-143°C

Lit. b.p. 142-143°C

Tripehnyltin bromide (Ph_3SnBr). This compound was prepared by mild bromination of tetraphenyltin by the pyridine-bromine addition compound at -48°C (Kraus[132]). The product was recrystallised from anhydrous ether.

Triphenyltin acetate ($Ph_3SnOOCCH_3$)

The preparation of this compound has been reported [133,134] by the reaction of triphenyltin hydroxide with glacial acetic acid. In the present work, two new methods of preparation for this compound have been developed.

(1) Equivalent proportions of triphenyltin chloride and silver acetate were reacted in anhydrous ether solution. The reaction mixture was shaken overnight. Silver chloride precipitated out and was filtered off in a dry box. The crude product obtained from the ether solution was recrystallised from petroleum ether. The infrared spectrumof this product showed the expected C=O absorptions and bands for monosubstituted benzene

groups.

(ii) In another experiment, triphenyltin acetate was prepared by refluxing equivalent quantities of tetraphenyltin and silver acetate in toluene for eight hours. Metallic silver separated out and the acetate was isolated from the toluene solution. The reaction product was recrystallised from ether. This procedure was followed from Anderson's method[73] for the preparation of a variety of alkyltin derivatives by the reaction of metallic acetates with tetra-organotins. It was found that the cleavage of the first C-Sn bond was easy, following which there was no subsequent cleavage of the C-Sn bonds. Attempts were made to prepare diphenyltin diacetate using an excess of silver acetate but the product obtained was the mono-acetate.

Analysis	Found	Calc. for $Ph_3SnOOCCH_3$
	C = 60.18	58.72
	H = 4.66	4.41

Triphenyltin trifluoroacetate ($Ph_3SnOOCCF_3$) was prepared by reacting triphenyltin chloride with an equivalent quantity of silver trifluoroacetate in anhydrous ether. The reaction mixture was shaken for 24 hours, silver chloride precipitated out and was filtered off in a dry box. The filtrate was evaporated on a vacuum line and the crude product was purified by recrystallisation from ether.

Diphenyltin bis-(trifluoroacetate, $Ph_2Sn(OOCCF_3)_2$ was prepared by refluxing .442 gm. tetraphenyltin and .442 gm. silver trifluoroacetate in toluene. The reaction mixture was heated for eight hours. Metallic silver separated out and the trifluoroacetato was isolated from the toluene solution. The product was recrystallised from anhydrous ether.

Diphenyltin, (Ph-Sn-Ph) (Kraus and Becker[136])

Phenylmagnesium bromide was prepared by reacting 2.5 gm. of magnesium turnings with 15.7 gm. bromobenzene in anhydrous ether (for details see Gatterman[137]).

Stannous chloride was made anhydrous by heating it at 100°C *in vacuo* for four hours. 9.5 gm. of the anhydrous stannous chloride was added in small portions into the phenylmagnesium bromide solution with continuous stirring. The colour of the reaction mixture changed to yellow and diphenyltin separated out. The yellow product was filtered and extracted with anhydrous benzene and the solution was dried over anhydrous sodium sulphate. The solution was poured into an excess of absolute alcohol when diphenyltin precipitated out as yellow crystalline product. The compound was filtered under an atmosphere of nitrogen and dried *in vacuo*.

Found	m.p.	~ 200°C decomposed
Lit.	m.p.	~ 205-6°C decomposed

Hexaphenylditin ($Ph_3Sn-SnPh_3$) was prepared according to the method of Kraus and Becker[136] by reacting triphenyltin chloride in xylene with sodium metal suspended in boiling xylene. The reaction was carried out in an atmosphere of nitrogen and under completely anhydrous conditions. Hexaphenylditin was recrystallised from anhydrous ether.

Conductivity measurements were carried out using a Wayne-Kerr Universal conductivity bridge. The solutions of hexaphenylditin and hexaphenyldilead were made up in nitromethane and measurements were made at different temperatures.

Tris(pentafluorophenyltin)fluoride, $(C_6F_5)_3SnF$ (Sharp and Winfield[138], tri-n-butyltin fluoride, Bu_3SnF (Sharp and Kemmitt[139]) and di-n-propyltin difluoride Pr_2SnF_2, (Sharp and Winfield[138]) were prepared by reacting sulphur tetrafluoride with tetrakis-pentaflurophenyltin at 120°C, tetra-n-butyltin at room temperature and tetra-n-propyltin at room temperature respectively. All the reactions were carried out in a stainless steel bomb.

Tetrakis-pentafluorophenyltin $(C_6F_5)_4Sn$ was a gift from Dr. R.D. Peacock of the University of Birmingham.

Table 14 Melting Points and Analysis Results for Phenyltin Compounds

Compound	Found M.P. °C	Lit. M.P. °C	Found C%	Found H%	Calc. C%	Calc. H%
Tetraphenyltin	224-5	225-6	66.51	5.08	67.49	4.69
Hexaphenylditin	236-7	237	62.58	4.64	61.77	4.30
Tetrakispentafluorophenyltin	215	221	35.90		36.61	
Tris-(pentafluorophenyl)tin fluoride	dec. ~340-57	dec. 345-57	33.21	F=47.10 Sn=19.39	33.81	F=47.59 Sn=18.58
Triphenyltin fluoride	dec. ~350	decomp. 357	57.43	4.35	58.58	4.07
Tri-n-butyltin fluoride	-	-	46.85	8.99	46.65	8.75
Bis-(n-propyltin)difluoride	-	-	28.48 28.66 33.04	6.03 5.95 5.44	29.66	5.76
Triphenyltin chloride	103-5	106-107	55.39	3.90	56.07	3.92
Diphenyltin dichloride	41-42	42		Cl=20.58		Cl=20.65
Triphenyltin bromide	119-120	120.5-122	51.02	4.11	50.27	3.49
Triphenyltin hydroxide	118-9	118-120	57.46	4.72	58.90	4.36
Bis-(triphenyltin)oxide	122-123	122-123.5	61.38	4.16 Sn=33.22	60.39	4.19 Sn=33.18

Table 14 (continued) Melting Points and Analysis Results for Phenyltin Compounds

Compound	Found M.P. °C	Lit. M.P. °C	Found C%	Found H%	Calc. C%	Calc. H%
Bis-(tri-n-butyltin)oxide			50.55	9.55	48.38	9.07
Triphenyltin acetate	121-2	121-2	58.16	4.75	58.72	4.41
x Triphenyltin trifluoroacetate	118-120		52.01	3.63	51.87	3.24
x Diphenyltin bis-trifluoroacetate	dec. ~ 250		38.55	2.38	38.50	2.01

- Compounds decomposed without melting.

x Compounds have not been described previously.

Infrared measurements:- The spectra in the sodium chloride region (2-15 μ) were recorded using a Perkin-Elmer Infracord or a Grubb Parsons Type S4 spectrophotometer. The spectra were obtained in Nujol and hexachlorobutadiene mulls, except for phenyltin trichloride and tetra-n-butyltin which were examined as liquid films. Spectra were taken between sodium chloride plates. Mulls were prepared under rigid 'drybox' conditions.

The range 650-200 cm^{-1} was recorded as Nujol mulls on a Grubb Parsons Model DM2 spectrophotometer fitted with caesium iodide optics. The samples were held between caesium iodide or polythene plates.

All figures are in cm^{-1} and letters have their usual significance.

CHAPTER II

THE INFRARED SPECTRA OF SOME PHENYLLEAD COMPOUNDS.

The work discussed in this chapter is a continuation of the work described in the preceding chapter. The organolead compounds prepared in the course of the present work are analogous with the corresponding organotin derivatives. The electronic configuration of lead is similar to that of tin. Both these elements form organometallic compounds with covalencies of two and four; the latter being more frequent than the former. Because of these similarities tin and lead form similar alkyl and aryl compounds. The organolead compounds are, however, more reactive than the organotin compounds and are thermally less stable as is expected from the increasing weakness and polarity of the Pb-C bond. The Pauling electronegativities of the Group IVA elements are given in Chapter I and Pb-C and Pb-halogen bonds are expected to have some ionic character.

The purpose of the present investigations was to try to establish the existence of aryl or alkyl lead cations.

In compounds of the type R_4Pb, the lead has a tetrahedral arrangement. The structure of these compounds has been confirmed by physico-chemical data. Electron diffraction investigations (Brockway and Jenkins[141]) have shown that the tetramethyl derivatives of lead possess a tetrahedral symmetry. Other workers[142-144] have determined the crystalline structure of tetraphenyllead by means of X-ray diffraction. In each of these cases the results agree

with the tetrahedral configuration and the bond distances correspond to covalent bonds. Electron diffraction measurements (Skinner and Sutton[145]) on liquid $(CH_3)_3Pb\text{-}Pb(CH_3)_3$ agree with the following parameters:-

Pb-Pb = 2.88 Å; Pb-C = 2.25 Å; $\angle$C-Pb-Pb = 109.5°

These calculations give probably the most accurate value for the covalent radius of lead. From the above discussion it is concluded that the organo-lead compounds are typically covalent compounds with a true tetrahedral configuration round the lead atom.

Organolead compounds, in which lead forms a bond with a highly electronegative or electropositive element or group are reported[101], in the previous literature, to be ionic salts. For example, the lead atom has been thought to be either in the cationic or in an anionic form in the following compounds: $(C_2H_5)_3P\overset{+}{b}Cl^-$, $(C_6H_5)_3Pb^-Li^+$. The compounds containing Ph_3Pb^- anions have not been isolated in crystalline forms, although they may be present as reaction intermediates in solution. However, there are many compounds which are reported to contain R_3Pb^+ cations. For instance, dipole moment measurements of the organolead halides have been found in the region expected for inorganic salts-e.g. NaI, 4.9;$(C_2H_5)_3PbBr$, 4.88; Ph_3PbCl, 4.3; $Ph_3PbC_2H_5$, 0.81 - indicating that the halogen-lead bonds are largely ionic in nature. (Malatesta, and Pizzotti[147]). More recently, Barbieri et.al.[148] have postulated the existence of $(C_2H_5)_3Pb^+$ and $(C_2H_5)_2Pb^{+2}$ cations in chloro complexes.

These workers have interpreted the ultraviolet spectrum of Ph_3Pb (oxinate) in terms of a salt-like structure containing Ph_3Pb^+ cations. However, the present work has shown that the phenyl lead compounds are covalent in nature. If the organolead cations did exist in some of the organolead derivatives, a planar configuration would be expected about the lead atom. It would be expected that the infrared spectrum would show some noteworthy changes, when a covalent organolead compound with a tetrahedral structure is converted into an organolead cation having a planar configuration. (cf. the spectral changes between Ph_4C and Ph_3C^+ cation[40]). In the course of the present work a variety of phenyllead derivatives have been prepared and their spectra examined. The infrared spectra of all these compounds are quite similar and are the characteristic spectra of a mono-substituted benzene group. The spectra of the phenyllead compounds are very similar to those of the analogous tin compounds and the spectra will be discussed in terms of separate phenyl and C_3MX or C_2MX_2 groups. The Pb-X vibrations occur in the very far infrared region and such vibrations have only been recorded in the spectrum of diphenyllead difluoride. Frequency assignments of the mono-substituted benzene groups are made according to Whiffen[31] and the results are shown in Tables 1-4. A complete analysis for the abosrption frequencies of the infrared spectrum of a representative member (tetraphenyllead) is shown in Figure I. The bands derived from the

Table I

Frequency assignments of Ph_4Pb and Ph_6Pb_2

Mode		Absorption frequencies (cm^{-1})	
Whiffen's notation	Description	Ph_4Pb	$Ph_3Pb-PbPh_3$
z	A_1 νC-H	3040m	3040m
k	A_1 νC-C	1563m	1563m
m	A_1 νC-C	1470s	1468s
n	B_1 νC-C	1425vs	1425vs
		1370w	1370w
c	B_1 νC-C	1319w	1319w
e	B_1 βC-H	1298m	1294w
		1252w	1253w
a	A_1 βC-H	1163w	1170w
c	B_1 βC-H	1143w	1149w
d	B_1 βC-H	1055s	1057m
b	A_1 βC-H	1016s	1012s
p	A_1 ring	994s	995s
j	B_2 γC-H	970w	970w

Table I

Frequency assignments of Ph_4Pb and Ph_6Ph_2

(continued)

Mode		Absorption frequencies (cm^{-1})	
Whiffen's notation	Description	Ph_4Pb	$Ph_3Pb-PbPh_3$
i	B_2 γC-H	907w	909w
g	A_2 γC-H	851w	851w
f	B_2 γC-H	727vs	725vs
v	B_2 ϕC-C	697vs	695s
s	B_1 αC-C-C	615w	-
y	B_2 X sens.	449sh,440vs	446sh,440vs
t	A_1 X sens.	222-b	222-b

Table 2 — Frequency assignments of phenyllead halides

Mode			Absorption frequencies (cm^{-1})				
Whiffen's notation		Description	Ph_2PbF_2	Ph_3PbCl	Ph_2PbCl_2	Ph_3PbBr	Ph_3PbI
z	A_1	νC-H	3035w	3040m	3035m	3035m	3040w
k	A_1	νC-C	1563m	1563m	1560m	1563w	1563m
m	A_1	νC-H	1471s	1471s	1471s	1466s	1466s
n	B_1	νC-C	1429vs	1429vs	1429vs	1425vs	1420vs
			1371w	1370w	1370w	1370w	1370w
o	B_1	νC-C	1325w	1318m	1319m	1318w	1316w
e	B_1	βC-H	1295w	1295m	1294m	1295w	1294w
c	B_1	βC-H	1155w	1152w	1150w	1149w	-
d	B_1	βC-H	1056m	1055s	1056s	1055m	1055m
b	A_1	βC-H	1016s	1010s	1012s	1012m	1010m
p	A_1	ring	994s	990s	990s	995s	990s
j	B_2	γC-H	961w	-	-	-	966w

Table 2 (continued)

Frequency assignments of phenyllead halides

Mode		Absorption frequencies (cm^{-1})				
Whiffen's notation	Description	Ph_2PbF_2	Ph_3PbCl	Ph_2PbCl_2	Ph_3PbBr	Ph_3PbI
i	B_2 γC-H	907w	905w	909w	-	-
g	A_2 γC-H	840w	-	840w	840w	848w
f	B_2 γC-H	729,719vs	734s,726s,716vs	725s,718vs	729s,719vs	725vs
v	B_2 ØC-C	686s	685s	690s	690s	688s
y	B_2X sens.	433vs	437s	435vs,442sh	437vs	442vs
		350-320b(Pb-F)				
t	A_1X sens.	230-220b	229w	-	~ 220-b	-

Table 3 **Frequency assignments of phenyllead acetates and trifluoroacetates**

Mode		Absorption frequencies (cm^{-1})			
Whiffen's notation	Description	$Ph_3PbOOCCH_3$	$Ph_2Pb(OOCCH_3)_2$	$Ph_3PbOOCCF_3$	$Ph_2Pb(OOCCF_3)_2$
z	A_1)C-H	3045m	3035w	3049w	3035w
				1667sh(C-O)	1656sh(C-O)
				1635vs(C-O)	1615vs(C-O)
k	A_1)C-C	1563sh	1575sh	1563w	1563w
		1536vs(C-O)	1545vs(C-O)		
m	A_1)C-C	1471m	1471m	1471m	1471m
n	B_1)C-C	1429vs	1433s	1431s	1431s
		1408s	1406s		
o	B_1)C-C	1335w	1333m	1325w	1323w
e	B_1 βC-H	-	-	1299w,1274w	1299w
				1192s(C-F)	1190vs(C-F)
a	A_1 βC-H	1169w	1174m	-	-
c	B_1 βC-H	-	1151s(C-F)	1155s(C-F)	1160s,1148s(C-F)
d	B_1 βC-H	1058w	1044w	1056w	1055w

Table 3 **Frequency assignments of phenyllead acetates and trifluoroacetates**

(continued)

Mode		Absorption frequencies (cm^{-1})			
Whiffen's notation	Description	$Ph_3PbOOCCH_3$	$Ph_2Pb(OOCCH_3)_2$	$Ph_3PbOOCCF_3$	$Ph_2Pb(OOCCF_3)_2$
b	A_1 δ C-H	1010m	1022s	1022m	1010m
p	A_1 ring	992m	995s	995m	990s
i	B_1 γC-H	906w	943m, 917w	-	-
g	A_2 γC-H	847w	-	848w	851sh, 844m
		-	-	800w, 794w	794m
		741sh	-	-	-
f	B_2 γC-H	732sh, 725vs	730vs	725vs	733sh, 721vs
v	B_2 ØC-C	692s	685s	687s	680s
s	B_1 αC-C-C	614w	-	-	-
y	B_2 X sens	466vs	445b	440s	441vs

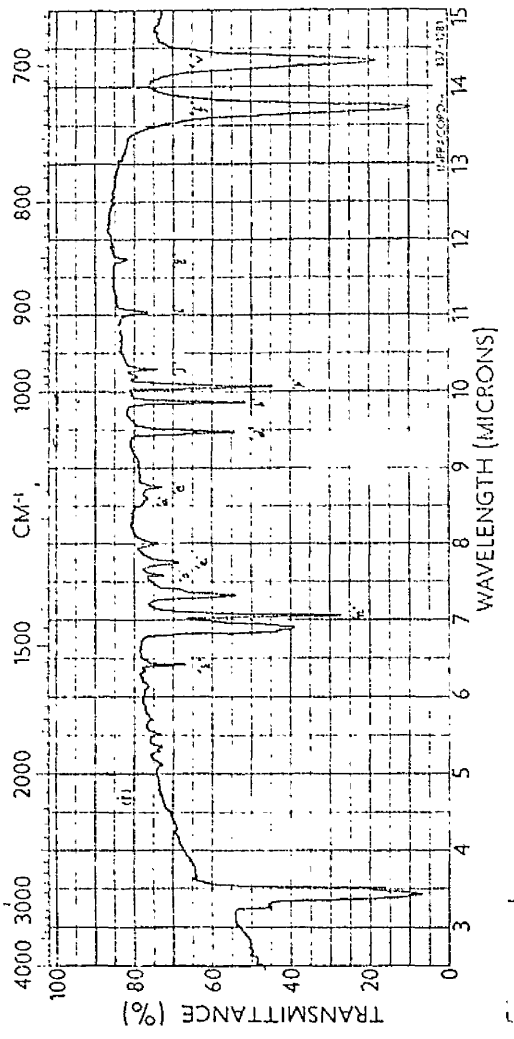
Table 4 — Frequency assignments of Ph_3PbOH

Mode			Absorption frequencies cm^{-1}
Whiffen's notation		Description	Ph_3PbOH
z	A_1	νC-H	3035m
k	A_1	νC-C	1563w
m	A_1	νC-C	1466m
n	B_1	νC-C	1420vs
			1370w
o	B_1	νC-C	1325w
e	B_1	βC-H	1290w
c	B_1	βC-H	1143w
d	B_1	βC-H	1055m
b	A_1	βC-H	1015m
p	A_1	ring	995s
i	B_2	γC-H	910w
g	A_2	γC-H	845w

Table 4 Frequency assignments of Ph_3PbOH

(continued)

Mode		Absorption frequencies cm^{-1}
Whiffen's notation	Description	Ph_3PbOH
f	B_2 γC-H	729vs, 722sh
v	B_2 ØC-C	694s
y	B_2 X sens	444s



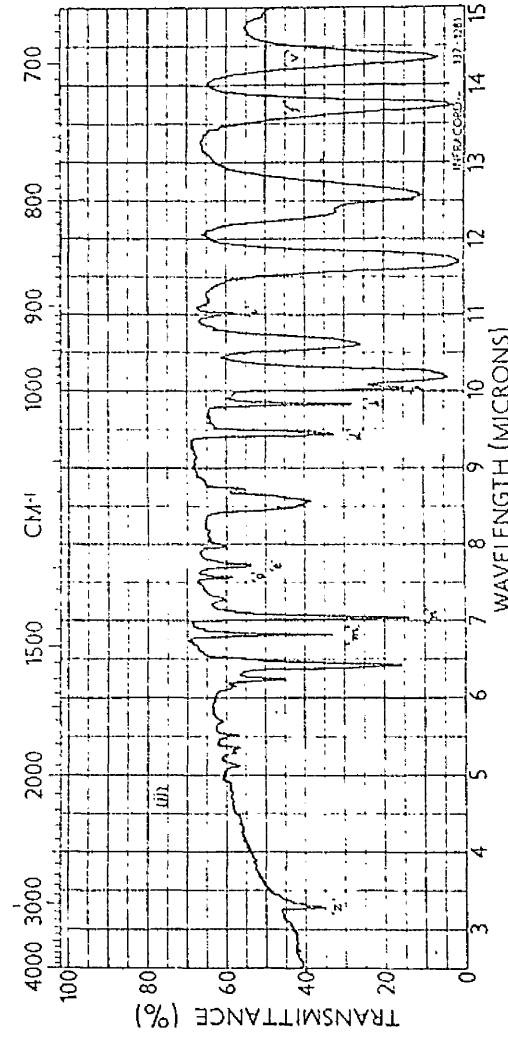


Fig. I (a) Infrared spectra of tetraphenyllead (i) in Nujol mull (ii) in hexachlorobutadiene mull.

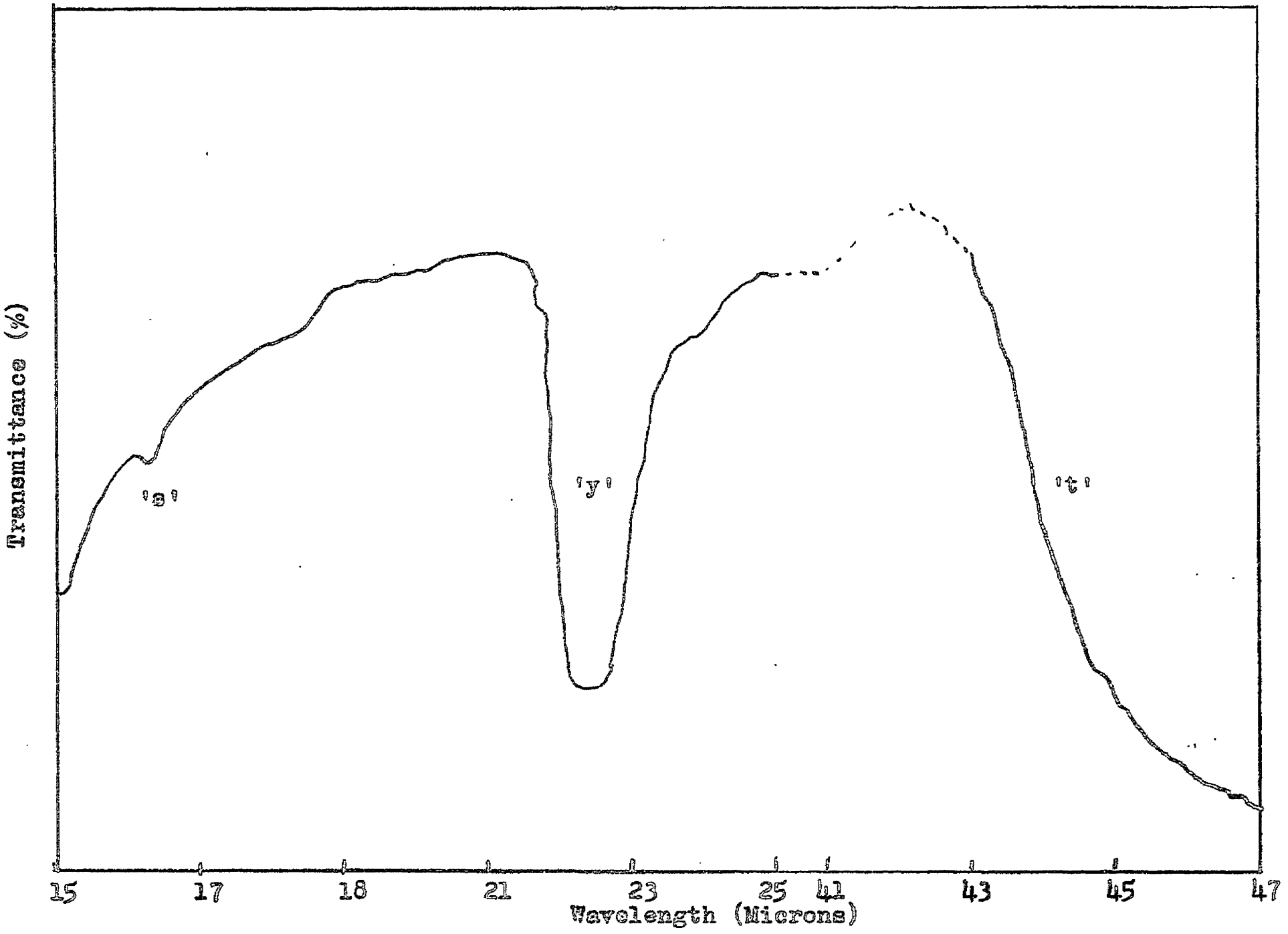


Figure 1(b) Infrared Spectrum of tetraphenyllead.

phenyl groups are discussed below:-

The vibrational frequencies of a mono-substituted benzene group are discussed in the introductory part of the preceding chapter. A weak to medium intensity band is observed near 3040 cm^{-1} in the spectra of all the compounds and is identified with Whiffen's 'z' band for a C-H stretching mode. The overtones and combination bands of the normal C-C modes are observed as four to five weak intensity bands in the 2000-1650 cm^{-1} region. The absorption bands near 1563, 1470, 1425 and 1320 cm^{-1} are identified as Whiffen's 'k', 'm', 'n' and 'o' vibrations arising from C-C vibrations of the phenyl groups. There are relatively stronger bands near 1295, 1170, 1150, 1055, 1016 cm^{-1} which are assigned to C-H vibrations and Whiffen's 'e', 'a', 'c','d' and 'b' modes.

The band near 1055 cm^{-1} has been reported[146] to be characteristic of phenyllead derivatives. We have noticed that the position of the band is little affected by different substituents on the lead atom. However, the intensity of this band decreases markedly in the spectra of the phenyllead acetates and trifluoroacetates. The corresponding band near 1070 cm^{-1} in the spectra of phenyltin acetates and trifluoroacetates showed a similar behaviour. The above observations are in agreement with the results obtained by Henry[149], who has reported a similar decrease in the intensity of this band in the spectra of aryllead acetates, aryllead arsonates and aryltin arsonates. From the above observations, it can be

said that, in general, a decrease in the intensity of the band is noticed where there are Pb-O or Sn-O bonds in organometallic compounds.

The symmetric ring vibration (Whiffen's 'p' mode) is readily assigned near 995 cm^{-1}. The absorption band is sharp in intensity and is shown by all the phenyllead derivatives. The strong intensity bands around 730 and 700 cm^{-1} are assigned to the out-of-plane C-H deformation modes (Whiffen's 'f' and 'v' bands). Splitting of one or other of these bands has been observed in the spectra of some of the aryllead compounds. (cf. the spectra of aryltin compounds). The shape of these absorption peaks may be used for distinguishing between different phenyllead derivatives. The splitting of these bands in the spectra of solid derivatives is probably due to crystal effect; either the situation of the molecule on the lattice sites of low symmetry, or the interaction of the molecule in the unit cell.

The band near 615 cm^{-1} is assigned as Whiffen's 's' band and is an in-plane ring deformation mode. The vibration does not involve the substituent to any large extent. The abosrption is usually of a very weak intensity and is only observed when the spectra are recorded in concentrated mulls.

Whiffen has recorded four substituent-sensitive vibrations (t,y,u,x) in the far infrared spectra of the

halobenzenes. The assignments for these frequencies in the spectra of phenyllead compounds are made on the basis of comparison with the assignments for the halobenzenes. The 't' and 'y' vibrations occur near 500 cm^{-1} when the substituents are lighter elements. The 't' band has been observed as a broad diffuse absorption near 220 cm^{-1}; the band was not observed in some cases where the band has shifted to slightly lower frequency because of the effect of electronegative groups attached to the lead atom and is out of the range of the spectrophotometer used in the present work.

The 'y' band was observed as a strong band near 440cm^{-1} in all the phenyllead derivatives. The band was often split, or had a shoulder and resembled the spectra of other aryllead derivatives studied by Harrah et.al.[28].

From the comparison with the results of Raman spectroscopy, Whiffen's 'x' and 'u' bands are expected to occur below 200 cm^{-1} for the phenyl derivatives of the heavier elements. Hence these vibration were not detected in the region examined for the phenyllead compounds.

Apart from the strong bands that have been identified, the compounds showed a number of weak intensity bands whose origin is unknown. These absorptions are presumably derived from combination modes of the monosubstituted benzene ring vibrations or of the C-Pb skeletal modes.

Structure of Specific Compounds:-

Hexaphenyldilead, $Ph_3Pb-PbPh_3$:-

The reactivity of $R_3Pb-PbR_3$ type of compounds is well known. Hexaphenyldilead adds[150] to the double bond in maleic anhydride to form an addition compound. Similarly, hexaphenyldilead is easily cleaved by phenyl lithium in ether to produce[151] Ph_3PbLi. The halogens and hydrogen halides react with organolead compounds containing Pb-Pb bonds and form R_3PbX, R_2PbX_2 and PbX_2 products. The auto-oxidation of hexacyclohexyldilead has been found[152] to occur photochemically under the influence of U.V. light. These properties show that Pb-Pb bond is relatively weaker than the Pb-C bond and the behaviour of this type of compound is similar to those of the solutions of triphenylmethyls. In view of these properties it was proposed[153] that R_6Pb_2 type of compounds were highly dissociated in dilute solutions to form free radicals of the type $R_3Pb^{\cdot}$. However, magnetic susceptibility measurements made on various compounds of this type did not show [122,123] paramagnetism. According to Malatesta[124], organolead compounds showed no indication of dissociation in high melting solvents.

In order to confirm the heterolytic dissociation of hexaphenyldilead, it was advisable to carry out conductivity measurements on this compound. In the present work, the measurements were carried out in nitromethane solution at varying temperatures. The conductivity results are shown in

the preceding chapter. It is concluded that the compound did not show any measurable heterolytic dissociation into ions.

The infrared spectrum of solid hexaphenyldilead is identical with that of tetraphenyllead. This indicates that hexaphenyldilead is a covalent compound and the pale yellow colour of the compound may be due to the presence of slight impurity of diphenyllead which may have been formed as a result of a disproportionation process.

The halides:-

The aryllead halides possess similar properties as the analogous tin compounds. For instance, the fluorides behave as ionic salts as they possess relatively low solubility and high melting points and some decompose without melting. The other halides are soluble in non-polar solvents and appear to be covalent in character.

In the present work, the infrared spectra of diphenyllead difluoride, triphenyllead chloride, diphenyllead dichloride, triphenyllead bromide and triphenyllead iodide have been examined. The spectra are similar to the spectrum of tetraphenyllead and are characteristic for the monosubstituted benzene ring vibrations. While discussing the infrared spectrum and crystal structure[54] of trimethyltin fluoride, in Chapter I, it was concluded that the spectra are in favour of a covalent model in which the three methyl groups lie in a single plane and are tilted with respect to Sn-F-Sn axis.

The tin atoms are five coordinate in this polymeric chain structure. From the similarities between the infrared spectra of organotin and organolead fluorides, it is suggested that the organolead fluorides also possess a predominently covalent structure and the structure involves five co-ordinate lead atoms. As regards the structure of the other halides, the spectra do not show any remarkable changes and are similar to that of the fluoride. Thus polymeric structures involving five co-ordinate lead atoms are preferred for the organolead chlorides, bromide and iodide.

The Pb-X vibrations:- These absorptions are expected to occur in the far infrared region. In the case of diphenyllead difluoride, a broad band is observed at 350-320 cm^{-1}. The absorption is assigned to a Pb-F vibration as no absorption in this region is observed in all the other phenyl lead halides. There has been no previous report of a Pb-F absorption in organolead compounds.

No extra absorption bands were observed in the spectra of the compounds containing Pb-Cl, Pb-Br and Pb-I groups. Such vibrations would presumably occur below 200 cm^{-1} outside the range of the present spectrophotometer.

Triphenyllead perchlorate:- This is a new compound and was obtained by reacting triphenyllead bromide with silver perchlorate in benzene solution. It was considered that since the perchlorate group is a very strong electronegative, there

would be a good chance of the formation of Ph_3Pb^+ ions in this derivative. The product showed a strong interaction with the solvent or moisture and was not obtained in a crystalline form. The infrared spectrum showed absorptions characteristic of triphenyllead group and strong bands at 1200-910 cm^{-1} for the perchlorate group. The absorptions of the perchlorate group are in favour of a bridging covalent structure, rather than an ionic structure similar to the organotin perchlorates.

Triphenyllead hydroxide:- The organolead hydroxides are frequently soluble both in organic solvents and in water. Trialkyllead hydroxides are fairly strongly basic in aqueous solution and such solutions are sufficiently alkaline to absorb carbon dioxide from air to form carbonates. Triethyllead hydroxide has been reported[101] as an ionic compound containing $(C_2H_5)_3Pb^+$ cations. Triphenyllead hydroxide is not water-soluble and is less basic in nature. If the hydroxide is ionic or Ph_3Pb^+ cations are formed by hydrolysis there should be changes in the spectrum as compared with the spectra of covalent aryllead compounds. In the present work, the infrared spectrum of triphenyllead hydroxide has been found similar to that of tetraphenyllead, and triphenyllead hydroxide is considered to be a covalent in the solid state. The spectrum of the hydroxide did not, however, show any absorption for an OH group. This is in agreement[154] with the absence of OH stretching vibrations in the hydroxides of the

heavier elements of Group IVA elements. The spectrum shows absorption at about 330 cm^{-1} which is not observed in other phenyllead derivatives and is assigned to a Pb-O vibration.

The acetates:- Phenyllead acetates and trifluoroacetates are soluble in organic solvents which probably indicates that the compounds are covalent in character. The C-O absorptions of the acetates are similar to those of the corresponding aryltin acetates. As discussed in the previous chapter, the C-O frequencies are expected to be similar to that of an ionic acetate e.g. sodium acetate when a C-O group is present as a bridge between two organometallic groups. The C-O absorption frequencies, as recorded in the present work, are shown in Table 5.

Table 5 C-O stretching frequencies cm^{-1}.

Compound	Asym. stretch	Sym. stretch
$Ph_3PbOOCCH_3$	1563sh, 1536vs	1408s
$Ph_2Pb(OOCCH_3)_2$	1575sh, 1545vs	1406s
$AgOOCCF_3$	1640s	*
$Ph_3PbOOCCF_3$	1667sh, 1635vs	*
$Ph_2Pb(OOCCF_3)_2$	1656sh, 1615vs	*

* absorption masked by Nujol or other bands.

In the trifluoroacetates, the C-O stretching frequencies are similar to those of silver trifluoroacetate which is a covalent bridged[155] compound. Thus from infrared evidence, the structures of phenyllead acetates and trifluoroacetates are

spectrum of phenylene oxide and methoxy-substituted phenylene oxide, the coalescent pyridine[138] compound. Some further evidence that the ease cyclize to those of ether carbonate might be found in the 2,6-dimethyl derivative and is assigned to a 2,6-di- absorption at about 730 cm^{-1} which is not observed in other phenylene elements of Group IVA elements. The absorption band

* absorption noted by Mojé as ether band.

Compound	Band, maxima	Intensity
$(C_6H_5)_3Si$	1260sh, 1255vs	1400s
$(C_6H_5)_2Si(OCH_3)_2$	1270sh, 1254vs	1405s
$C_6H_5Si(OCH_3)_3$	1260s	*
$(C_6H_5)_2Si(OCH_3)_2$	1261sh, 1253vs	*
$(C_6H_5)_3Si$	1258sh, 1251vs	*

Table 3. C-O Absorption Frequencies[a]

Table 3

trends" as assigned by Mojé are given in Table 3.

Ranges between two oxygen atoms, The C-O absorption band at 1260 cm^{-1} is assigned as a "C-O coupling" band in the present chapter, The C-O vibrations are expected to be similar to ethyl or aromatic ethers. As discussed in the previous chapter, the C-O

Type assignment- Phenylsilyl acetates and trialkyl acetates are similar to those of silver trialkylacetate *which has* two simple carboxylate groups which produce symmetric and antisymmetric

suggested as similar to those of the analogous phenyltin derivatives. The compounds are covalent in nature and carboxylate groups are probably present as bridges.

The C-F vibrations:- The assignments for the C-F vibrations of the phenyllead trifluoroacetates are made according to Randle and Whiffen[95] who have studied the characteristic C-F stretching modes of the CF_3 group. They have observed the C-F absorptions near 1180 cm^{-1} and near 1140 cm^{-1}. The corresponding C-F absorptions for the trifluoroacetates prepared in the present work are shown in Table 6.

Table 6

C-F stretching frequencies cm^{-1}.

Compound		
$AgOOCCF_3$	1198vs,	1150s, 855s, 800s, 735s,
$Ph_3PbOOCCF_3$	1192s,	1155s, 848w, 800w, 794w,
$Ph_2Pb(OOCCF_3)_2$	1190vs	1160s, 1148s, 844m, 794m,

Miscellaneous reactions:-

Reaction of triphenyllead bromide with aqueous Hydrofluoric acid or sodium fluoride.

The organometallic fluorides are relatively less soluble than the other halides. As described in the previous chapter, triphenyltin fluoride was easily obtained by reacting triphenyltin chloride with aqueous hydrofluoric acid. The

preparation of triphenyllead fluoride was attempted by reacting aqueous hydrofluoric acid with triphenyllead bromide in an alcoholic solution, but the reaction product was characterised as diphenyllead difluoride and not as the expected triphenyllead fluoride. In a further attempt, triphenyllead bromide was reacted with sodium fluoride in ethanol solution, but the product obtained was again characterised as diphenyllead difluoride.

The formation of the difluoride could result from a disproportionation reaction of the mono-fluoride formed in the course of the reaction or as a result of further attack of hydrofluoric acid on triphenyllead fluoride.

Reactions of Phenyllead halides with silver acetate or trifluoroacetate.

In the course of present work, a new technique has been developed for the preparation of phenyllead acetates and trifluoroacetates by working in non-aqueous solvents. The aryllead halides (other than the fluorides) react with the silver acetate or trifluoroacetate and the organolead acetates and trifluoroacetates are obtained in good yields. Triphenyllead trifluoroacetate and diphenyllead bis-trifluoroacetate are new compounds. The compounds were characterised by infrared spectroscopy and analysis.

Experimental

All the previously known compounds were prepared by the literature methods. The reactions were carried out under anhydrous conditions wherever necessary. The compounds were characterised by carbon and hydrogen analysis and by melting point determinations. Tetraphenyllead was used as a starting material for most of the phenyllead derivatives and was obtained from Light and Co. Ltd. and was recrystallised from benzene before use.

Hexaphenyldilead, $Ph_3Pb-PbPh_3$ was prepared according to the method of Gilman and Baillie[156] by reacting triphenyllead iodide with sodium. The product was recrystallised from benzene and dried *in vacuo*. Found m.p. the compound decomposed at about 150° C without melting.

Analysis

	Found	Calc for Ph_6Pb_2
C =	48.43%	49.27%
H =	3.68%	3.42%

Conductivity measurements on Hexaphenyldilead were made as described in the preceding chapter.

Triphenyllead chloride, Ph_3PbCl was prepared by reacting tetraphenyllead with hydrogen chloride gas in chloroform (Gilman and Robinson[157]).

Found	m.p.	204-206°C
Lit.	m.p.	206°C

Analysis.

Found	Calc. for Ph_3PbCl
C = 46.35	45.60
H = 3.25	3.16

Diphenyllead dichloride, Ph_2PbCl_2

This compound was prepared by the same method as described for triphenyllead chloride.

Found m.p. decomposed without melting.

Lit. m.p. decomposes at 284-286°C without melting.

Analysis.

Found	Calc. for Ph_2PbCl_2
C = 33.29	33.41
H = 2.66	2.33

Triphenyllead bromide, Ph_3PbBr:- was prepared by slow addition of bromine in pyridine to tetraphenyllead suspended in pyridine, both reagents being cooled to -50°C (Gruttner[158])

The product was recrystallised from benzene.

Found	Calc. for Ph_3PbBr
C = 42.10	41.69
H = 3.27	3.00

Triphenyllead iodide, Ph_3PbI was prepared by reacting tetraphenyllead with iodine (Gilman and Baillie[156]).

The compound was recrystallised from benzene.

Found m.p. 135-137° C

Lit. m.p. 138-139° C

Analysis

Found	Calc. for Ph_3PbI
C = 38.26	38.23
H = 3.02	2.57

Diphenyllead difluoride, Ph_2PbF_2:- Triphenyllead bromide was dissolved in warm alcohol and an excess of aqueous hydrofluoric acid was added to the alcoholic solution. On keeping the solution overnight a crystalline product was obtained which analysed to diphenyllead difluoride.

In another attempt, triphenyllead iodide was reacted with sodium fluoride in alcoholic solution. The insoluble product obtained was identified as diphenyllead difluoride.

m.p. The compound decomposed before melting.

Analysis

Found	Calc for Ph_2PbF_2
C = 37.11	36.07
H = 2.52	2.51

Triphenyllead perchlorate Ph_3PbClO_4

Triphenyllead bromide was reacted with an equivalent proportion of anhydrous silver perchlorate in benzene solution. Silver chloride precipitated out and was filtered off in a dry box. The filtrate was evaporated under vacuum and an oily product was obtained. The compound was not obtained in a crystalline form and was not characterised by analysis.

Triphenyllead hydroxide Ph_3PbOH was obtained by hydrolysis of triphonyllead chloride with potassium hydroxide, (Bähr[159]). The product was recrystallised from alcohol and dried under vacuum.

Analysis

Found	Calc. for $(C_6H_5)_3PbOH$
C = 47.83	47.43
H = 3.93	3.52

Preparation of triphenyllead acetate, $(C_6H_5)_3PbOOCCH_3$:-

The preparation of this compound has been reported (Austin [135]) by the reaction of acetic acid on triphenyllead hydroxide. In the present work, equivalent proportions of triphenyllead bromide and silver acetate were reacted in an alcoholic solution. The solution was shaken overnight. Silver chloride precipitated out and was filtered off and the solution evaporated to obtain the acetate which was recrystallised from ethanol. Found m.p. 205-207°C, Lit. m.p. 206-207°C.

Found	Calc. for $Ph_3PbOOCCH_3$
C = 48.01	48.27
H = 3.86	3.65

Diphenyllead diacetate $Ph_2Pb(OOCCH_3)_2$

The compound was prepared using a similar method as used for the preparation of triphenyllead acetate.

4.32 gm. of diphenyllead dichloride was reacted with 3.34 gm. of silver acetate in ethanol solution. The reaction solution was shaken for 12 hours. Silver chloride was separated out which was filtered off and the diacetate was

obtained by evaporating the filtrate. The product was recrystallised from ether.

Found m.p. 195° C

Lit. m.p. 200-201° C

Analysis

Found	Calc. for $Ph_2Pb(OOCCH_3)_2$
C = 40.39	40.08
H = 3.57	3.37

Triphenyllead trifluoroacetate $Ph_3PbOOCCF_3$:-

.474 gm. of triphenyllead chloride was reacted with .221gm. of silver trifluoroacetate in ether solution. The reaction mixture was shaken overnight and then the insoluble silver chloride was filtered off. The filtrate was evaporated under vacuum and the crude product was recrystallised from ether. The compound decomposed before melting.

Analysis

Found	Calc. for $Ph_3PbOOCCF_3$
C = 44.53	43.55
H = 2.75	2.72

Diphenyllead bis-(trifluoroacetate), $Ph_2Pb(OOCCF_3)_2$

4.31 g. (.0043 mole) diphenyllead dichloride and 4.42g. (.0088 mole) silver trifluoroacetate were reacted in ether solution while the reaction mixture was shaken overnight. Silver chloride separated out and the trifluoroacetate was

isolated from the ether solution. The product was recrystallised by dissolving in ether and adding an excess of petroleum ether. The compound was dried *in vacuo*.

Analysis:-

Found	Calc. for $Ph_2Pb(OOCCF_3)_2$
C = 32.68	32.69
H = 1.66	1.70

Infrared measurements:- The infrared spectra were recorded as described in the preceding chapter.

CHAPTER III

THE FAR INFRARED SPECTRA OF SOME PHENYL DERIVATIVES OF GROUP IVA, VA, VIA AND VIIA ELEMENTS.

The vibrational spectra of mono-substituted phenyl derivatives have been extensively investigated[28,31,160,161] but little has been reported on the far infrared (650 to 200 cm^{-1}) spectra of these compounds. In the present work, more complete spectral data on a series of phenyl derivatives of groups IVA to VIIA elements are presented. The spectra are interpreted in detail and complete assignments are made for the stronger bands.

Plyler[160] has suggested that there should be eight theoretically possible modes of vibrations for a mono-substituted benzene ring, which would be expected to give absorptions in the region 650-150 cm^{-1}. He recorded the infrared spectra of a number of halobenzenes and alkyl substituted benzenes in the 15-40 μ region. The maximum number of absorption bands, observed in the spectra of these compounds, was five and some of these absorption bands were Raman active. Some other workers[28,31,161] have also observed that the number of observed absorption bands for a mono-substituted benzene group in the far infrared region is much lower than expected from simple theory. The total number of observed infrared bands should depend on the complexity and overall symmetry of the molecule[162-164].

The most comprehensive study of the infrared and Raman spectra of monosubstituted benzene derivatives is by Whiffen[31]. He has described various modes of vibration for a monosubstituted benzene group and his nomenclature is followed in discussing the results obtained in the present work. The infrared spectra of most of the compounds reported in this work, have apparently been recorded by Harrah et.al.[28], but they have only published the results graphically and detailed frequency assignments are not given.

Frequency assignments are made according to Whiffen[31] and the position of bands are recorded according to vibrational assignments in the Tables 1-5. The compounds are designated by the symbol of the atom attached to the benzene rings.

Table I — Whiffen's 's' vibration

F	Cl	Br	I	
610	614	614	618	
O	S	Se		
617	606	610		
N	P	As	Sb	Bi
615	615	617	617	621
C	Si	Ge	Sn	Pb
625	618	618	618	615

Table 2 Whiffen's 't' vibration

F	Cl	Br	I	
518	417	312	[266R]	
O	S	Se		
562	406	321		
N	P	As	Sb	Bi
512 shoulder	429,418	311,305	272,267	232,220
C	Si	Ge	Sn	Pb
521	431	325	256	222

Table 3 Whiffen's 'y' vibration

F	Cl	Br	I	
495	467	455	448	
O	S	Se		
495,476	518,465	479,454		
N	P	As	Sb	Bi
500	510,494	470	451	450,437
C	Si	Ge	Sn	Pb
490	510	460	455,448	448

Table 4 Whiffen's 'u' vibration

F	Cl	Br	I	
404	302,295	244	219	
O	S	Se		
394	260(very broad)	244(very broad)		
N	P	As	Sb	Bi
431,405	249,242	-	-	-
C	Si	Ge	Sn	Pb
412	268,235,216	269,222	-	-

Table 5 Whiffen's 'x' vibration

F	Cl	Br	I	
243	[196R]	[181R]	-	
O	S	Se		
244	-	-		
N	P	As	Sb	Bi
241	-	-	-	-
C	Si	Ge	Sn	Pb
240,233	-	-	-	-

All frequency values are in cm^{-1} and are those recorded in the present investigation except those values placed within parenthesis. In these latter cases absorption bands are not observed, and the values reported in this work are from Whiffen[31]. The frequencies, recorded for halobenzenes, are in complete agreement with those collected by Whiffen[31]. In the present work, for the phenyl derivatives other than halobenzenes, vibrational assignments are made for all the observed bands by comparison with the spectra of halobenzenes; that is, treating all the compounds as derivatives of mono-substituted benzene rings and neglecting the vibrations due to the central skeleton of the molecule. Deacon and Green[165] have also reached the same conclusion from a detailed study of the infrared and Raman spectra of the phenyl derivatives of Group VA elements.

In the region studied, except for a possible complication in the spectra of diphenyl oxide and triphenylamine, there is a straightforward one to one correlation between the bands observed in the infrared spectra of the halobenzenes and the bands observed in the infrared spectra of the other phenyl derivatives of Groups IVA, VA and VIA elements. To explain the anamolous features in the spectra of diphenyl-oxide and triphenylamine, it is suggested that vibrational coupling between the different phenyl groups attached to the 'central' atom is most likely to occur when the

'central' atom is light and there is conjugation between the phenyl groups across the 'central' atom. Such conjugation involves a lone pair of electrons on the 'central' atom and the π-electron systems of the benzene rings and is postulated[162-164,166,167] for diphenyloxide and triphenylamine. The effects of this type of conjugation are reflected in the far infrared spectra of diphenyloxide and triphenylamine as they show slightly anomolous features. Such conjugation results in a frequency shift or band intensity change as described in the following discussion.

There should be five fundamental vibrations in the far infrared region (650-200 cm^{-1}) of a simple mono-substituted benzene (Whiffen[31]). The highest frequency occurs at about 620 cm^{-1} (Whiffen's 's' band) and is a B_1 class in-plane ring deformation mode (Whiffen's symmetry classifications refer to idealised mono-phenyl derivatives). This absorption varies in intensity in the spectra of different compounds. In lighter elements the absorption is sharp or medium intensity while the phenyl derivatives of heavier elements normally show a weak intensity band and in some cases the band is only observed in a concentrated mull. The vibration does not involve the substituent to any extent and the frequency of this absorption is not at all sensitive to the substituent.

Whiffen records a substituent-sensitive vibration of symmetry A_1 to occur between 520 and 266 cm^{-1} in the infrared spectra of the halobenzenes (vibration 't'). Following these assignments the corresponding vibrations may be identified in the spectra of the other phenyl derivatives as shown in Table 2. For the lighter elements both the 't' and 'y' vibrations occur with frequencies near to 500 cm^{-1}. In the spectra of the halobenzenes the intensity of the 't' vibration is much less than that of the 'y' vibration and hence the assignments have been made on the basis of intensity. This assignment gives an unexpectedly high frequency for the 't' vibration (observed at 562 cm^{-1}) in diphenyl oxide and this may be associated with the interaction between the lone pair of electrons on the oxygen atom and the π-electron system of the phenyl rings[162-164,166,167]. In the case of triphenylamine there is also a strong interaction between the lone pair of electrons on the nitrogen atom and the π-electron systems of the phenyl groups but the position of band (at 512 cm^{-1}) is as expected for other compounds.

The assignment of other bands observed in the infrared spectra is quite straightforward and has been made on the basis of comparison with the spectra and assignments of the halobenzenes. Whiffen's 'y' band occurs between 500 and

437 cm^{-1} and is from a B_2 class vibration. This band is often split and the spread of values follows closely the graph of Harrah et.al.[28]. Whiffen's 'u' vibration of class B_1 occurs between 430 and 200 cm^{-1}. The band is often split and broadened and could not always be identified in the spectra of derivatives of the heavier elements. Whiffen's 'x' vibration of class B_2 was observed for the carbon, nitrogen, oxygen and fluorine derivatives at 240, 241, 244 and 243 cm^{-1} respectively. The absorption at 241 cm^{-1} in the case of triphenylamine is of exceptionally strong intensity as compared to those of other compounds. The anomolous behaviour of triphenylamine may be explained on the basis of a strong interaction between the lone pair of electrons on nitrogen and π-electrons of the phenyl groups. Chlorobenzene and bromobenzene were found to show 'x' vibrations at 196 and 181 cm^{-1} as Raman active bands. Thus by comparison with the results from Raman spectroscopy, this vibration would be expected to occur below 200 cm^{-1} for the phenyl derivatives of heavier elements.

In most cases, the infrared bands show the marked splitting which has also been observed by previous workers. The splitting of bands occur in the spectra of solid derivatives and it is concluded that it arises from the crystal effects, either the situation of the molecules on lattice sites of low symmetry or interaction of the molecules in the unit cell. Apart from the strong bands that have been identified as originating from fundamental

vibrations, each spectrum contained a number of minor peaks, that appear to be derived from combination modes. No assignments have been attempted for these bands.

EXPERIMENTAL

Most of the compounds were obtained from commercial sources and were recrystallised or redistilled before study. Fluorobenzene (C_6H_5F) was obtained by thermal decomposition of benzene diazonium fluoroborate which was prepared according to the method of Nuttall and Sharp[168].

15 g. of freshly distilled aniline was dissolved in 15 ml. concentrated sulphuric acid. The solution was cooled by ice and a slurry was obtained. A solution of 11 g. sodium nitrite in 50 ml. water was added to the above slurry with continuous stirring. To avoid diazo-amine coupling the reaction flask was cooled to 0° C and cracked ice was added to the slurry. After diazotization, the amine went into solution. The fluoroborate was obtained by adding the diazotised solution, in sulphuric acid, to 40% aqueous fluoroboric acid. The fluoroborate was precipitated and was filtered and dried. The fluoroborate was decomposed by heating it in a glass tube fitted with a U trap. Flurobenzene, formed as a decomposition product of the fluoroborate, was collected in the trap cooled by solid carbon dioxide and acetone mixture. Fluorobenzene was further purified by distillation under vacuum.

Tetraphenylmethane, (Ph_4C) was prepared according to the method of Gomberg and Cone[169] by reacting phenylmagnesium bromide with triphenylchloromethane. The reaction product was a mixture of triphenylmethane, triphenylcarbinol, triphenylmethyl peroxide and tetraphenylmethane. The first

two compounds are soluble in ether while the peroxide and tetraphenylmethane separated out as insoluble products. The crystalline product was filtered off and tetraphenylmethane was extracted with benzene. The yield of the product obtained was as low as 5% because of the side reactions and also the steric factors involved in the preparation of this compound.

Found m.p. 282-284° C.

Lit. m.p. 285° C.

Analysis

Found	Theory for Ph_4C
C = 92.95	93.75
H = 6.42	6.25

Tetraphenylgermane (Ph_4Ge) was kindly donated by Organisch Chemisch Institut T.N.O., Utrecht, Holland. The compound was recrystallised from benzene before use.

Found m.p. 233° C

Lit. m.p. 233.4° C.

Tetraphenylsilane (Ph_4Si) was kindly donated by Nobel Division of Imperial Chemical Industries Ltd. The compound was recrystallised from benzene and dried *in vacuo*.

Found m.p. 235-236° C

Lit m.p. 235-237° C

Analysis

Found	Calc. for Ph_4Si
C = 85.01	85.65
H = 6.16	5.95

The far infrared measurements were carried out as described in Chapter I.

CHAPTER IV

SPECTROSCOPIC STUDIES ON TRIARYL CARBONIUM ION COMPOUNDS AND THEIR COMPLEXES

A. General Introduction

The existence of triarylcarbonium ions in solution as well as in solid salts is at present a firmly established fact. One method[40] of preparing such compounds is through the reaction:

$$Ar_3CCl + AgX \longrightarrow AgCl + Ar_3CX$$

where X is an anion of a very strong acid. The factors which influence the ionisation of an Ar_3CX entity are as follows. The process is

$$Ar_3\ C{:}X \longrightarrow Ar_3C^+ + X^-$$

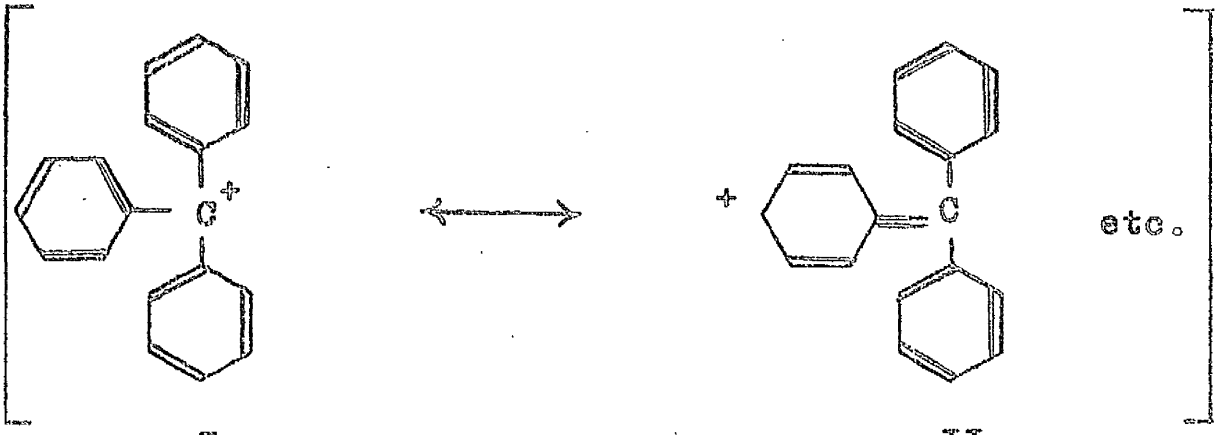
The reaction will be favoured if the C-X bond is weak. Thus ionisation will occur more readily in iodides (C-I bond strength 57.4 k.cals) than in fluorides (C-F bond strength 105.4 k.cals). Pauling[96(a)]. The value of the C-X bond strength is greatly dependent[170] upon the presence of electron attracting or electron repelling groups subsituted into the aryl rings. Hence the ionic or covalent nature of the Ar_3CX molecule will depend upon the substituents present in the ring system. The effect of substituents is also allied to the stability of the triaryl-carbonium ions; in general, electron releasing substituents, e.g. alk_2N groups, tend to stabilise the carbonium ions as in the case of triphenylcarbonium ion dyestuffs. The presence of an electron withdrawing substituent is expected to stabilise

the covalent model. The anion will also effect the ionisation of the Ar_3CX molecule through its basicity. Anions derived from strong acids will favour the ionisation whereas anions from weak acids will favour a more covalent structure. The final decision as to whether triphenylmethyl derivatives are covalent or ionic is a balance of all the factors discussed above. Triphenylchloromethane is covalent but on successive substitutions of electron-releasing p-methoxy groups in the rings, the compound becomes ionic on the substitution of the fourth methoxy group (Lund[171]). Tri-p-methoxy phenylchloro-methane is covalent but if the basicity of the anion is slightly decreased by the formation of HCl_2^- ion, an ionic derivative is formed[172]. The present work was designed to provide further evidence on the actual factors which determine the boundry between ionic and covalent compounds.

Structure of triarylcarbonium ion:- Organic compounds with a four co-ordinate carbon atom have the tetrahedral arrangement of valencies associated with sp^3 hybridisation. Carbonium ions can be regarded as derivatives of a carbon atom which has given up one of the valency electrons and the remaining electrons are present as hybrids of the sp^2 type with a planar trigonal disposition of the bonds attached to the 'central' carbon atom. The most stable carbonium ions are obtained where the π-orbitals of the organic groups attached to the 'central' carbon atom form an overlap with the vacant p-orbital on the carbon atom.

Examples of such ions with an increasing order of stability are $(CH_2 = CH = CH_2)^+ < PhCH_2^+ < Ph_2CH^+$ and $< Ph_3C^+$ (Bethell and Gold[138]).

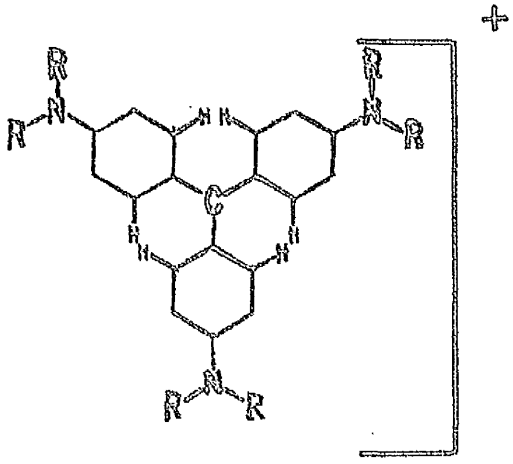
The triarylcarbonium ions can be visualised to exist in a number of resonance forms in which the 'central' carbon atom becomes doubly bonded.



I II

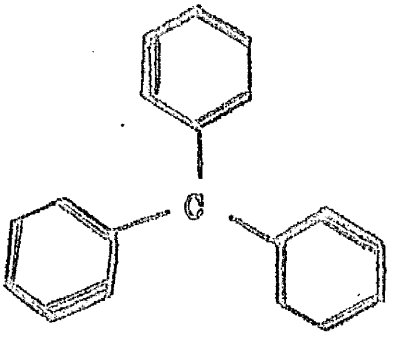
The mesomeric stabilisation of a conjugated system is most effected when all the π-bonds lie in the same plane (Dewar[173]). All of the benzene rings are, therefore, required to be coplanar in order to get the maximum resonance stabilisation. The molecular orbital approximation makes the same prediction (Leffler[174]). The vacant p-orbital of the 'central' carbon atom is perpendicular to the plane of the the three sp^2 bonding orbitals and all the benzene rings have to be coplanar if the 'central' p-orbital is to overlap to the maximum extent with the π-orbitals of the adjacent rings. Calculations based on known bond lengths and Vand Der Waal radii indicate that in a planar configuration of the triphenylcarbonium ion, steric interference would occur between the ortho-hydrogen atoms on

adjacent phenyl groups. The structure of crystal violet cation is shown below.

III  R = CH_3

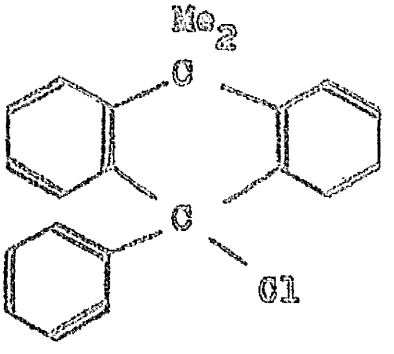
The atomic distances are approximately to scale. Because of the steric interference of the ortho-hydrogens, Lewis, Magel and Lipkin[175] proposed a structure in which each of the benzene ring is twisted out of the plane which contains the three bonds to the 'central' carbon atom. Deno, Jaruzelski and Schriesheim[176] have estimated the angle of twist required by this model as high as about 50° . It is possible that the ion exists in two isomeric forms, one corresponding to a symmetrical propeller and the other to a propeller in which one of the benzene rings has been tilted the wrong way. Such isomerism was predicted by Lewis, Magel and Lipkin[175] who interpreted the absorption spectrum of crystal violet ion in terms of these two structures. It was found[177] however, that there was no evidence for such isomerism in the spectrum of triphenylmethyl free radical. The infrared studies (Sharp and Sheppard[40]) of crystalline triphenyl-carbonium complexes have provided a strong support for a propeller-like structure of Ph_3C^+ ion. The authors have

ruled out the unsymmetrical structure of the cation and the confirmed picture of the triphenylmethyl carbonium ion is shown in Structure IV in which all the three phenyl groups are twisted in a symmetrical fashion.



IV

Simple molecular orbital calculations on the π-electron energies of triphenylcarbonium ion have demonstrated[178] that the resonance involves all rings and twisting of the rings does not reduce the resonance energy to a large extent. The above conclusion is also consistent with the ionisation measurements of compounds of the type shown in Structure V, in which two of the phenyl groups are constrained to approximate coplanarity (Bartlett[179]) and in which the resonance energy of the carbonium ion could be higher than in a propeller shaped ion.



V

The present work includes a study of three carbonium ion dyestuff compounds.

Malachite green, phenyl bis-p-N-dimethylaminophenylmethyl;

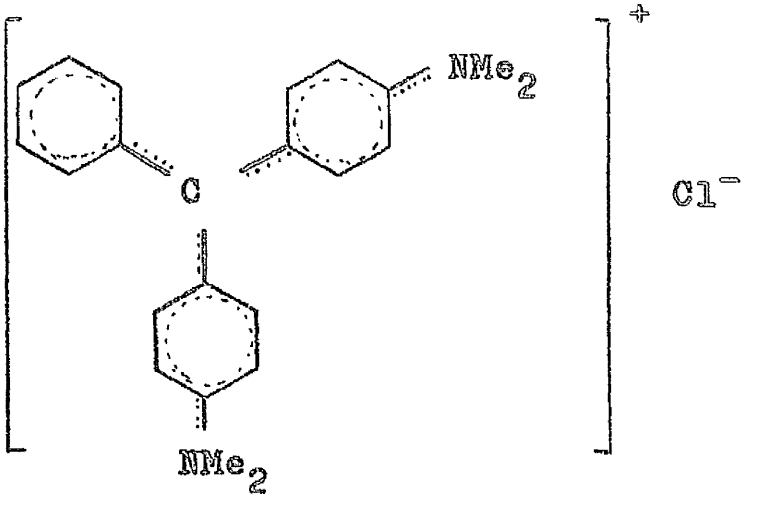
Brilliant green, phenyl bis-p-N-ethylaminophenylmethyl;

Crystal violet, tris-p-N-dimethylaminophenylmethyl.

These dyestuffs are normally obtained in the form of their chlorides which are highly coloured and contain triphenylcarbonium ions. The crystal violet cation is symmetrical in shape (See structure III) while the malachite green and brilliant green cations are unsymmetrical and are shown below.

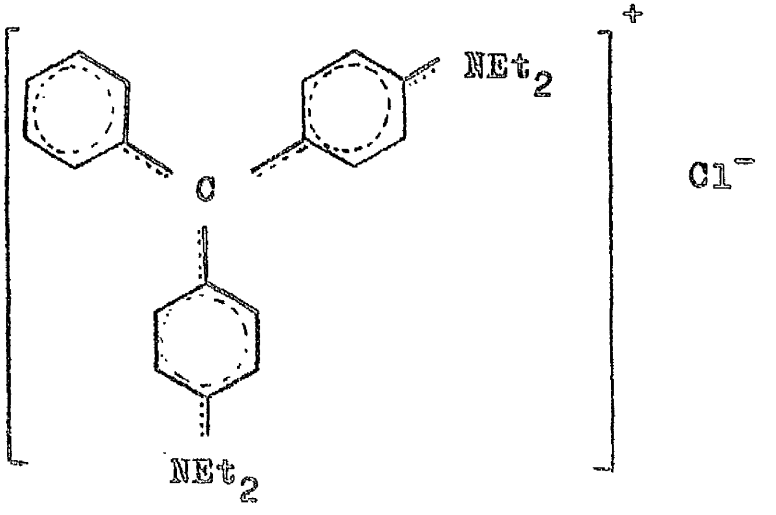
Malachite green

VI



Brilliant green

VII



B. Spectral investigations on triarylcarbonium ion dyestuffs and their complexes in aqueous solution.

The relationship between colour and constituion of triphenylmethyl carbonium ion dyes has been discussed by various workers[175,180-182]. According to Lewis and Calvin[181], the absorption spectrum of a substance with a planar or almost planar molecule should consist of bands corresponding to electronic oscillations along three perpendicular axes of the molecule. The shorter the axis, the shorter the wavelength of its absorption. This suggestion was supported by Lewis and Bigeleisen[183] by studies on several basic dyes. In the ion of crystal violet (Structure III) which has a centre of symmetry, polarizability is the same in all directions of the plane, so that the 'x' and 'y' bands coincide and only one absorption band is observed at λ_{max} 598 m.μ. in the visible region. No band is observed for the 'z' axis. On the other hand, malachite green and brilliant green cations (structures VI and VII) are unsymmetrical and there are two well defined bands in the visible region at λ_{max} 430, 620 m.μ. and λ_{max} 433, 628 m.μ. respectively. If it is assumed that the major band in the crystal violet cation is due to an electronic oscillation in one direction, it may be stated that roughly 2/3 of the positive charge will be available for the uniaxial oscillation, while greater charge will be available for the corresponding oscillations in the malachite green and brilliant green cations. This explains the absorption spectra of triphenylcarbonium

dyestuffs in general.

The major absorption bands in the spectra of these dyes show remarkable changes with the changes in concentration or temperature. This has been explained[184-187] on the basis of aggregation of the dye cations in solution. In the visible spectra of these salt-like dyestuffs, the major band is associated with a shoulder which has been attributed to the presence of associated aggregates. Schubert and Levine[185] have polstulated a qualitative theory of metachromacy and the dye solutions are suggested to be a set of equilibria of several cationic species, e.g.

$$D^{+} \rightleftharpoons D_2^{++} \rightleftharpoons D_3^{+++} \rightleftharpoons D_4^{++++} \rightleftharpoons \quad \text{etc.}$$

The proportions of different polymeric forms depend upon the dye concentration. However, the monomeric species is predominantly present in dilute solutions and with the increase of concentration, the dimeric species is formed. It has been suggested that the dye cations are packed face-to-face with a layer of water molecules between each pair. This phenomenon of aggregation of the dye cations has recently been shown[188] to exist even in solvents of low polarity.

The nature of forces that are responsible for the association of the charged dye cations of the same sign has not been finally elucidated. According to some authors[184,189], the association is brought about by forces of Van Der Waals type while other workers[190,191] consider that hydrogen bonding brings about the aggregation. It seems

more likely, however, that polymerisation involves the π -electrons of the combining dye cations, imposing constraints such that the energy difference between the ground state and the first excited state is successively greater for the dimeric species and for each polymeric form. The heteropoly acids of tungsten and molybdenum form complexes with the dyes and the spectra are changed and it appears that aggregation or another process producing a similar electronic effect has become much more important in the dyestuff salts of the heteropoly acids. The following heteropoly acid anions were used in the present work: $[PMo_{12}O_{40}]^{3-}$, $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[FeW_{12}O_{40}]^{5-}$ and $[ZnW_{12}O_{40}]^{6-}$. The octahedral groups MoO_6 or WO_6 are linked together by sharing oxygen atoms to form a polyhedral closed basket like structure[192] and the four triply shared oxygen atoms are placed at the corners of a central tetrahedron. The hetero atom sits in the centre of this tetrahedron in the heteropoly ions.

Attempts to study the stoichiometry of the dye-heteropoly acid complexes were made spectrophotometrically in dilute solutions using Job's method of continueous variations. The complexes precipitated out when the dyestuff and the acid were mixed in proportions of the charges of the heteropoly acid anions and the dye cation.

The solution spectra of the dyestuff-heteropoly acid complexes are almost of the same pattern as those of the

dyes in concentrated solutions. The absorption peaks are much broader and are of much lower intensity as compared with those of the parent dyestuff solutions. The details of the solution spectra of these dyes and their complexes are shown in Table I. One significant feature of the spectra of crystal violet complexes is the shift of the major peak from the phosphomolybdate complex to the tungstozincate complex i.e. the greater the charge on the counter anion, the shorter the wavelength and the greater the energy difference between the ground and first excited level. The spectra of crystalviolet-heteropolyacid complexes are shown in Figure I. Since, the heteropoly anions are of large size and carry negative charges (-3 to -6), it seems likely that the dyestuff cations will tend to lie along the surface of the anions. Thus a progressive increase in charge density on the surface of the anion will have an increased effect on the π-bonding system of the dyestuff cations which would result in the progressive shifting of λ_{max} absorption. Such shifts are not observed in the spectra of malachite green and brilliant green complexes. Most probably these shifts may be masked, as the absorption peaks are diffuse and much broader in shape.

Table I

Spectra of the dyes and their complexes in aqueous solutions (400 - 700 mμ)

Dyestuff	Malachite green	Brilliant green	Crystal violet
chloride dilute solution	430,575sh,<u>620</u>	433,580sh,<u>628</u>	560sh,<u>598</u>
chloride conc. solution	430,<u>600</u>,630sh	430,<u>600</u>,640sh	<u>550</u>,600sh
Fluoroborate dilute solution	425,575sh,<u>620</u>	433,580sh,<u>630</u>	570sh,<u>620</u>
Fluoroborate conc. solution	425,<u>600</u>,630sh	complex precipitates out	-
Phosphomolybdate	440,<u>590</u>,640sh	440,<u>605</u>,640sh	<u>560</u>,630sh
Phosphotungstate	435,<u>590</u>,640sh	440,<u>605</u>,640sh	<u>550</u>,610sh
Silicotungstate	440,<u>585</u>,640sh	440,<u>605</u>,640sh	<u>575</u>,620sh
Tungstoferrate	440,<u>592</u>,610sh	440,<u>605</u>,645sh	<u>535</u>,620sh
Tungstozincate	440,<u>595</u>, -	440,<u>605</u>,645sh	<u>520</u>,620sh

Major peaks are underlined.

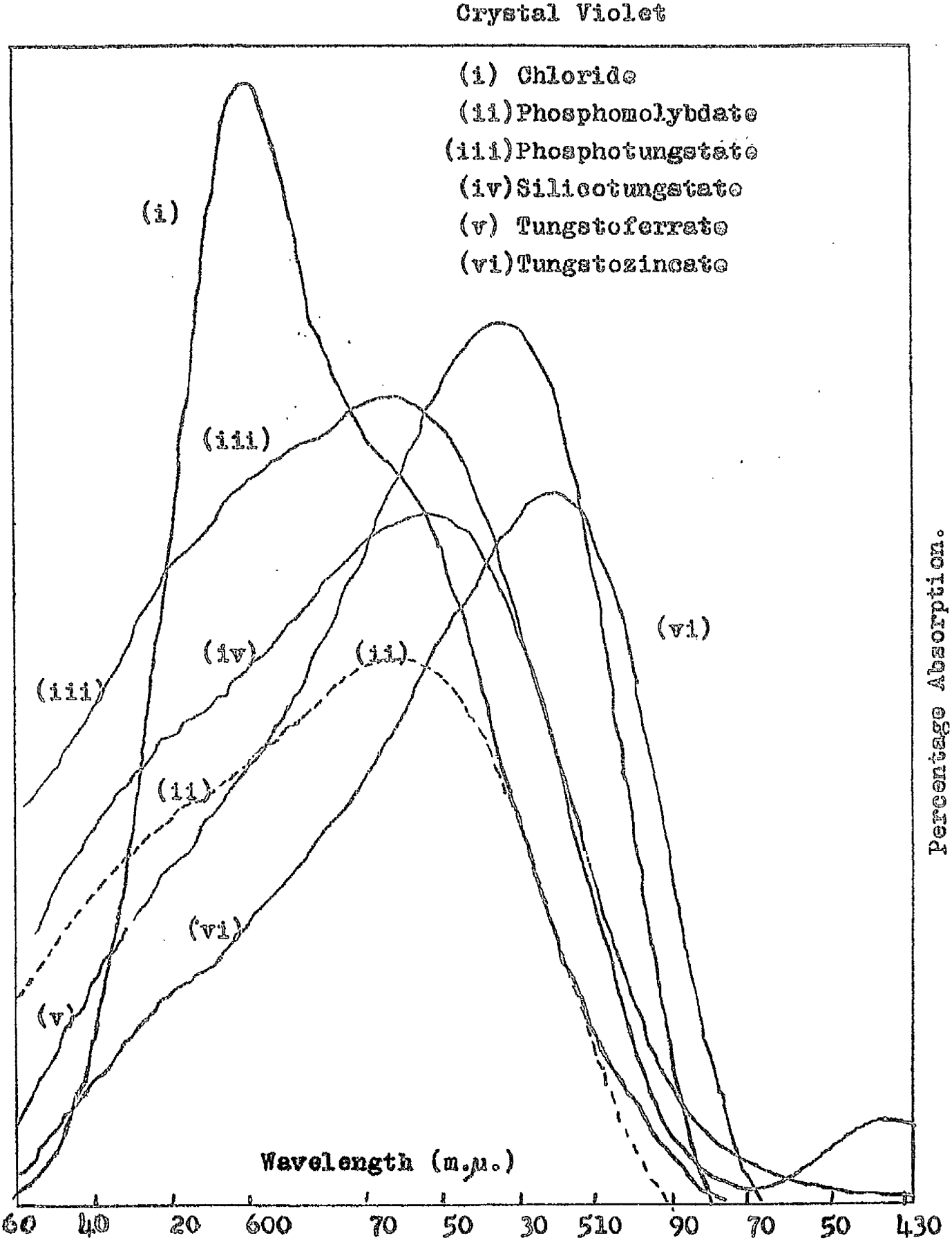


Fig. I. Absorption spectra of Crystal violet-heteropoly acid Complexes in aqueous solutions.

Experimental

Purification of dyestuffs:- The dyes were obtained from commercial sources and were recrystallised three times from 3/2 v/v ethanol-water mixture; after two recrystallisations the apparent molar extinction coefficients did not increase, and this was taken to indicate complete removal of impurities.

Heteropolyacids:- Phosphomolybdic acid, phosphotungstic acid and silico tungstic acid were obtained as commercial products in a pure form and tungstoferric acid and tungstozincic acid were prepared by Dr. D.H. Brown. The latter two acids were recrystallised from water before use.

Spectrophotometric measurements were carried out using an Optica or Hilger spectrophotometer. The solutions were made in distilled water. The spectra of the dyes were recorded in different known concentrations and the spectra of the dyestuff derivatives were obtained by mixing 3 ml 10^{-4}M dye solution with 9 ml or excess of 10^{-4}M KBF_4 or heteropoly acid solution. For Job's plot determinations, mixtures were made with variable compositions and pH was adjusted to be the same for each composition.

C. Solid carbonium ion salts of dyestuff compounds.

When concentrated solutions of the dyestuffs are mixed with concentrated solutions of sodium or potassium fluoroborate, perchlorate or heteropoly acids, sparingly soluble salts of the dyestuff cations separate out. A series of insoluble salts of malachite green, brilliant green and crystal violet have been prepared with anions of different charges. The stoichiometry of the dyestuff complexes precipitated from aqueous solutions was determined by analysis. The details of the analysis of these products are given in Table 3. The composition of the heteropoly acid complexes does not correspond to that of the complexes studied in dilute solutions. The stoichiometry of the solid complexes seems to depend on the size and charge of the heteropoly anions. Some water of crystallisation has always been found associated with these compounds. The solid derivatives are sparingly soluble in acetone and contain the parent dyestuff cations as determined by spectroscopic measurements of these solutions. The reflectance spectra of the solid derivatives are recorded in the visible region (400 - 700mμ).

The spectra of the fluoroborates and perchlorate are similar to t ose of the parent dyestuffs. In heteropoly acid complexes the absorption peaks are broader and it is often difficult to discriminate between the major peak and the shoulder. The spectra seem to be determined by the stoichiometry. From Table 3, it can be seen that the

Table 2

Reflectance Spectra 400 - 700 mμ.

Strongest peaks are underlined

Dyestuff	Malachite green	Brilliant green	Crystal violet
Chloride[-1]	430, <u>600</u>, 650sh	430, 585sh, <u>635</u>	<u>600</u>
Fluoroborate[-1]	430, 580sh, <u>640</u>	440, 590sh, <u>640</u>	<u>620</u>
Perchlorate[-1]	433, 600sh, <u>635</u>	435, 600sh, <u>640</u>	<u>600</u>, 660sh
Phosphemolybdate[-3]	440, 590sh, <u>630</u>	460, 500sh, <u>640</u>	432, <u>600</u>, 655sh
Phosphotungstate[-3]	440, 590sh, <u>640</u>	445, 590sh, <u>645</u>	595 broad
Silicotungstate[-4]	440, 590sh, <u>640</u>	445, 605sh, <u>638</u>	440, 615sh, <u>660</u>
Tungstoferrate[-5]	440, 585sh, <u>640</u>	440, 610sh, <u>645</u>	<u>600</u> broad
Tungstozincate[-6]	440, 590sh, <u>640</u>	445, 590sh, <u>645</u>	610 broad

heteropoly acid complexes do not conform to a uniform pattern of composition. In the case of phosphomolybdates all three dyestuffs form 3:1 complexes and the reflectance spectra resemble those of the parent dyes and their fluoroborates or perchlorates, where complexes are formed with different compositions, some spectral changes are recorded (See Table 2).

The infrared spectra of all the dyestuff derivatives show a very close resemblance to the spectra of the parent dyestuffs, the spectra being characteristic of the dye cations. Thus the ionic nature of these compounds has been demonstrated. The details of the spectra are given below and the bands originating from the anions are written within brackets.

Experimental

The compounds were prepared by mixing the concentrated solutions of the dyestuffs and the complexing agents in aqueous solution. On mixing the two solutions, highly coloured products separated out, and these were filtered and dried under vacuum.

Reflectance spectra were recorded on a Hilger spectrophotometer fitted with a reflectance attachment. The compounds were diluted by grinding them with anhydrous magnesium oxide or potassium chloride.

Estimation of non-volatile components A known weight of the complex was ignited in a weighed crucible. The residue

again. The phosphomolybdates were decomposed at 500-550° C in a muffle furnace.

The infrared spectra were recorded in Nujol and hexachlorobutadiene mulls using a Grubb Parsons spectrophotometer.

Table 3

Complexes Precipitated From Aqueous Solution

M.G. = Malachite Green B.G. = Brilliant Green C.V. = Crystal Violet

Complex	Non-volatile component Found%	Non-volatile component Theory%	Found C%	Found H%	Theory C%	Theory H%	Charge on Anion	Stoichiometry Dye : Anion
M.G. Fluoroborate			65.29	6.32	66.37	6.01	1	1:1
B.G. Fluoroborate			65.23	6.69	65.69	6.79	1	1:1
C.V. Fluoroborate			62.88	7.09	62.92	6.7	1	1:1
M.G. Perchlorate			64.91	6.04	64.30	5.83	1	1:1
B.G. Perchlorate			65.15	6.85	65.65	6.88	1	1:1
C.V. Perchlorate			62.74	6.59	62.43	6.45	1	1:1
M.G. Phosphomolybdate	56.11	56.10	21.36	2.24	21.46	2.37	3	3:1
B.G. Phosphomolybdate	64.29	64.38	23.54	3.03	24.13	2.86	3	2:1
C.V. Phosphomolydate	67.94	67.92	22.96	2.74	22.89	2.52	3	2:1
M.G. Phosphotungstate	69.23	69.31	18.21	2.01	18.67	2.51	3	3:1
B.G. Phosphotungstate	70.35	69.00	21.29	2.71	21.13	2.46	3	3:1
C.V. Phosphotungstate	69.00	69.05	24.66	2.89	22.33	2.33	3	3:1
M.G. Tungstosilicate	74.07	73.60	20.20	2.75	20.12	2.52	4	3:1
B.G. Tungstosilicate	73.09	72.59	20.54	2.53	21.77	2.56	4	3:1
C.V. Tungstosilicate	76.49	76.60	13.75	2.33	14.32	2.95	4	2:1
M.G. Tungstoferrate	72.02	72.22	21.12	1.92	21.27	1.97	5	3:1
B.G. Tungstoferrate	71.29	70.52	21.04	2.72	22.92	2.85	5	3:1
C.V. Tungstoferrate	58.56	58.56	29.82	3.19	30.09	3.29	5	5:1
M.G. Tungstozincate	68.99	68.95	22.07	2.39	21.03	2.08	6	3:1
B.G. Tungstozincate	70.28	70.16	21.84	2.95	22.58	2.97	6	3:1
C.V. Tungstozincate	63.91	64.01	23.38	3.23	24.82	3.51	6	4:1

Infrared spectra of malachite green and its derivatives:-

*Absorptions due to traces of moisture

Compound	Absorption frequencies cm^{-1}.
Dyestuff (Chloride)	3448w*, 1724w, 1587w, 1485w, 1450w, 1380s, 1220w, 1170m, 940m, 900w, 830w, 750w, 725s, 700w.
Fluoroborate	1616sh, 1585s, 1470w, 1440w, 1355s, 1220w, 1170s, 1055-1030b (BF_4^-), 940m, 902w, 830w, 750w, 730s, 700w.
Perchlorate	1616sh, 1583s, 1475w, 1445w, 1360s, 1220w, 1170s, 1188b (ClO_4^-), 943w, 905w, 835w, 750w, 725m, 699w.
Phosphomolybdate	1610sh, 1590m, 1470w, 1445w, 1365m, 1170m, 1055m, 950m, 885bw, 800w, 720m,
Silicotungstate	3509w*, 1615sh, 1585w, 1440w, 1335s, 1330w, 1170s, 1010m, 968s, 920vs, 880w, 795vs, 725m, 700w,
Phosphotungstate	1610sh, 1580vs, 1471w, 1441w, 1366vs, 1212w, 1168s, 1075s, 975s, 938w, 893s, 812sb, 725m, 699w,

Infrared spectra of malachite green and its derivatives:-

*Absorptions due to traces of moisture.

Compound	Absorption frequencies cm^{-1}
Ferritungstate	3448w*, 1613sh, 1577s, 1471w, 1441w, 1364s, 1212w, 1165s, 950m, 877s, 770sb, 725m,
Zincitungstate	3430w*, 2899w, 1610sh, 1577s, 1471w, 1433w, 1361vs, 1215w, 1166m, 940m, 877s, 752b, 725w.

Brilliant green and its derivatives

Compound	Absorption frequencies cm^{-1}.
Dyestuff chloride	1620sh, 1570s, 1430s, 1400s, 1352s, 1265s, 1180s, 1150s, 1065m, 996m, 920m, 885m, 840s, 798w, 765w, 750w, 700s,
Fluorob rate	1590sh, 1570s, 1476m, 1400w, 1350m, 1260m, 1212w, 1186s, 1150s, 1065-1025b (BF_4^-), 990m , 960w, 920m, 885m, 840m, 826w, 798m, 765w, 750w, 700s,

Brilliant green and its derivatives

Compound	Absorption frequencies cm^{-1}.
Perchlorate	1587s, 1480w, 1370s, 1351m, 1275m, 1220w, 1190s, 1156s, 1085m, 1070s (ClO_4^-), 1000w, 935w, 909w, 890w, 840m, 800w, 725w,
Phosphomolybdate	3448w*, 1615w, 1563m, 1460m, 1408w, 1389w, 1337m, 1266w, 1220m, 1180m, 1150m, 1050s, 954s, 872m, 798s, 715w,
Phosphotungstate	1709w, 1618w, 1585vs, 1449w, 1412s, 1389m, 1342s, 1269s, 1220w, 1190vs, 1163s, 1082vs, 980vs, 900s, 820b, 750w, 715m, 704w,
Silicotungstate	3520w*, 3020w*, 1600w, 1560m, 1430w, 1400w, 1372w, 1330m, 1255w, 1205w, 1178m, 1150w, 1065w, 1005m, 965s, 915vs, 885w, 795b,
Ferri tungstate	3448w*, 3030w, 2703w, 1613m, 1610s, 1471w, 1429m, 1390w, 1350m, 1282m, 1220w, 1190s, 1155s, 1075m, 1010m, 952vs, 877vs, 770b, 720w,

Brilliant green and its derivatives

Compound	Absorption frequencies cm^{-1}.
Zinci tungstate	3448w*, 2994w, 1613w, 1587s, 1449w, 1408w, 1389w, 1342w, 1275w, 1220w, 1190m, 1150m, 1075w, 1015w, 943s, 877s, 758b, 704w,

Crystal violet and its derivatives

Compound	Absorption frequencies cm^{-1}.
Dyestuff (chloride)	1577m, 1470w, 1351m, 1273w, 1219w, 1162m, 1000b, 938m, 909w, 830w, 719m, 695w,
Fluoroborate	1587s, 1485w, 1362s, 1278w, 1221w, 1169s, 1052b (BF_4^-), 938m, 909m, 833m, 757w, 740w, 719m, 695w.
Perchlorate	2865w, 1582s, 1471w, 1355s, 1290w, 1220w, 1176m, 1087m, 940w, 908w, 833w, 719 .

Crystal violet and its derivatives

Compound	Absorption frequencies cm^{-1}.
Phosphomolybdate	3448w*, 1585m, 1470w, 1351m, 1220w, 1173m, 1062m, 956s, 881m, 787b, 721w,
Phosphotungstate	2899w*, 1695w, 1536vs, 1506w, 1471m, 1344vs, 1282s, 1220w, 1156vs, 1070m, 971s, 935m, 890s, 826s, 806vs, 741w, 719s,
Silicotungstate	3440w*, 1612w, 1579m, 1470w, 1370m, 1220w, 1165m, 1010m, 917s, 881sh, 806-790b, 720w,
Ferri tungstate	2940w, 1695w, 1587vs, 1470w, 1360s, 1290w, 1220w, 1175s, 1060w, 943s, 910m, 870s, 830w, 794s, 740w, 719m,
Zinci tungstate	1700w, 1563vs, 1515w, 1471w, 1351s, 1282m, 1220w, 1163vs, 940m, 909w, 877m 830w, 793m, 755b, 719m,

D. Preparation of some covalent derivatives of carbonium ion dyestuffs.

It has already been mentioned at the beginning of this chapter, that the nature of triphenylmethyl derivatives depends upon the substituents in the phenyl groups and the basicity of the anions. Triphenylmethyl chloride is a colourless compound and is covalent, while the triphenylmethyl dyestuff chlorides are ionic because of the electron-releasing N-alkyl substituents. The dyestuff derivatives (as described in section C) of the heteropoly acid anions and other anions derived from strong acids, have been shown to be salt-like compounds and contain triphenylmethyl cations. The anions of weaker acids have a tendency to form covalent compounds. According to Leffler[174], the order of ionic character for a given carbonium ion is as follows:

hydroxide, alkoxide, and carboxylate < cyanide < thiocyanate < ferrocyanide < azide < chloride < bromide < sulphate and perchlorate. According to the kinetic and equilibrium studies of Gigen et.al.[193-195] the carbonium ion dyestuff cations are represented by a set of equilibria between colourless and coloured forms. The addition of an appropriate anion may change the equilibrium towards colourless or coloured species. For example, an aqueous solution of malachite green is rapidly decolourised when it is mixed with a borate solution. The decolourisation of the dye solution is due to the complex formation, and the

triphenylmethyl cation is changed into a covalent structure. Crystal violet and malachite green derivatives with cyanide, borate and sulphide anions have been reported[175] to be covalent in character and to contain pyramidal structures. From the above examples, it was proposed to prepare a series of covalent derivatives with anions of weaker acids and to confirm their structure by comparing their infrared spectra with those of the leuco bases of the carbonium ion dyestuffs. These are covalent compounds having a true tetrahedral arrangement of phenyl groups about the 'central' carbon atom.

Cyanides, cyanate, thiocyanate, azide, metaborate, and sulphide derivatives were prepared and their infrared spectra examined.

The Infrared spectra of all these dyestuff derivatives with anions of weak acids show close resemblance to the spectra of the leuco bases of these dyestuffs. The compounds particularly resembled at ca 2900 and 2800 cm^{-1} and the observed bands are from C-H vibrations of the N-alkyl groups. From infrared evidence, it is concluded that the derivatives are covalent with a tetrahedral arrangement about the 'central' carbon atom. The details of infrared data are given as follows.

Details of infrared spectra

M.G. = Malachite green.

B.G. = Brilliant green.

C.V. = Crystal violet.

≋ = Absorptions due to moisture.

Split peaks are underlined.

M.G. leuco base:- 2875s, 2795s, 1880w, 1610vs, 1515vs, 1473w, 1443m, 1345vs, 1295w, 1250w, 1220s, 1200w, 1185w, 1165w, 1125w, 1058m, 1025w, 945s, 860w, 820w, 814vs, 780w, 758w, 740m, 715m, 700s.

M.G. cyanide:- 2875s, 2795s, 2245w(C-N str.), 1890w, 1610vs, 1560w, 1515vs, 1485m, 1445s, 1351vs, 1325sh, 1299w, 1220m, 1205m, 1179w, 1165m, 1124w, 1058m, 1029w, 945s, 895w, 814vs, 764m, 758m, 740s, 725w, 699vs.

M.G. cyanate:- 3448≋w, 2865m, 2793m, 1606s, 1575s, 1515s, 1472w, 1445m, 1350s, 1215w, 1162m, 1124sh, 1055w, 1010w, 942w, 812s, 763m, 720m, 697m.

M.G. thiocyanate:- 3280≋w, 2890s, 2793s, 2273w, 1895w, 1610s, 1580sh, 1514s, 1473w, 1445s, 1350vs, 1215-1225m, 1056m, 1015w, 1010w, 985w, 943m, 812vs, 762s, 735m, 721m, 695s.

M.G. azide:- 2880m, 2793m, 1905w, 1610s, 1582s, 1513s, 1475w, 1445m, 1350s, 1215w, 1163s, 1125w, 1053w, 1010w, 943m, 813s, 763m, 738sh, 723m, 698m.

M.G. metaborate:- 2865m, 2793m, 2041w, 1953w, 1600s, 1575sh, 1513vs, 1475w, 1440m, 1350s, 1312w, 1466m, 1225s, 1125, 1005s, 971m, 943m, 930w, 913w, 810s, 790w, 763w, 731m, 719w, 694m.

M.G. sulphide:- 3390^{w}, 2872m, 2793m, 1600s, 1575s, 1511s, 1470w, 1439m, 1351s, 1214w, 1043s, 1121w, 1053w, 1030w, 940s, 900w, 812m, 797m, 761w, 748w, 722m, 697m.

B.G. leuco base:- 2905s, 2825m, 1916w, 1610vs, 1563w, 1513vs, 1485s, 1460w, 1435w, 1389m, 1355m, 1340m, 1266s, 1194m, 1155w, 1428w, 1384m, 1352w, 1336w, 1263m, 1193w, 1154m, 1080m, 1010w, 816m, 759m, 725m, 699m.

B.G. cyanide:- 2900vs, 2820s, 2240w (C-N str.), 1850w, 1615vs, 1565w, 1520vs, 1490vs, 1450w, 1425m, 1380s, 1350m, 1335m, 1260s, 1192m, 1154m, 1078m, 1010w, 980w, 815s, 759m 724m, 700m.

C.V. leucobase:- 2905s, 2793m, 1595m, 1515s, 1473w, 1441w, 1345s, 1280w, 1220m,1220w, 1160m, 1090w, 1054w, 1018w, 965w, 935w, 812m, 699m.

C.V. cyanide:- 2898s, 2793m, 2260w (C-N str.), 1590m, 1508s, 1474w, 1445w, 1351s, 1282w, 1225w, 1204w, 1156m, 1092w, 1055w, 1020w, 963w, 938w, 809m, 715m.

Experimental

Preparation of leuco bases.

Malachite green leuco base $C_6H_5CH(C_6H_4NMe_2)_2$, was obtained according to the method of Gatterman[137] by fusing together zinc chloride, dimethylaniline and benzaldehyde on a water bath. The leuco base was crystallised from alcohol.

Brilliant green leuco base $C_6H_5CH(C_6H_4NEt_2)_2$, was prepared by a procedure similar to that described for the preparation

of malachite green leuco base. The proportional amounts of diethylamine and benzaldehyde were reacted at 100°C in the presence of $ZnCl_2$ or conc. HCl. The product was recrystallised from alcohol.

Crystal violet leuco-base, $CH(C_6H_4NMe_2)_3$.

(Gattermann and Schnitzspahn[197]). Sesquichlorohydrate of hydrocyanic acid (2HCN+3HCl) was obtained by passing dry HCl gas through hydrogen cyanide cooled at -15 C. HCN was prepared by reacting sodium cyanide with conc. sulphuric acid. On reacting with HCl, a crystalline product was separated out and was dried, and was heated with dimethylaniline at 120-130°C. The product was crystallised from aqueous alcohol.

Preparation of dyestuff derivatives:- The carbonium ion dyestuffs were dissolved in water and mixed with sodium or potassium salts of anions of the weakly basic acids. On mixing the two solutions almost colourless products were separated out, and these were filtered off and dried under vacuum. In a few cases gummy materials were obtained and it was found difficult to obtain these products in colourless and crystalline forms. The cyanide derivatives were obtained in colourless forms by repeated recrystallisations as described by Calvert and Rechen[196]. The C and H analyses are shown in the following table.

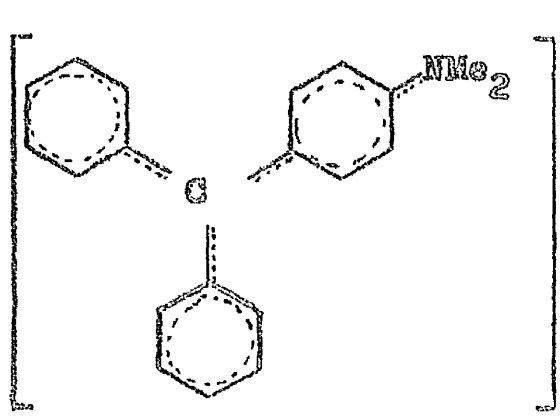
Table 4 — Analysis results

Compound	Found		Calculated		Dye cation/anion
	C%	H%	C%	H%	
M.G. leuco base	84.49	7.46	83.64	6.66	
M.G. cyanide	81.28	6.82	81.13	7.04	1:1
M.G. cyanate	77.35 78.61 77.10	6.71 8.97 6.90	76.88	6.96	1:1
M.G. metaborate	76.5	7.15	74.23	6.72	1:1
B.G. cyanide	80.28	7.47	81.75	8.02	1:1
C.V. leuco base	77.19	9.32	76.72	8.50	
C.V. cyanide	77.08	7.96	78.19	7.53	1:1

E. Dyestuff complexes precipitated from concentrated hydrochloric acid.

Malachite green, brilliant green and crystal violet give orange-red solutions in conc. HCl and it has been concluded [183,198] from ultraviolet and visible absorption spectra that carbonium dyestuffs are protonated in acid solutions. The changes in colour can be explained by successive protonation of the N-alkyl groups of the dye cations, this protonation ties down the lone pair of electrons on the nitrogen atoms. For example the crystal violet solution changes to green with the addition of a few drops of hydrochloric acid. The green colour is due to the protonation of one of the $N\text{-}Me_2$ groups and the cation becomes similar to malachite green cation (Structure VI). When protonated a second time the crystal violet cation becomes orange coloured. The successive protonation has tied down the lone pair of electrons on two nitrogen atoms giving a structure analogous to the malachite green cation and to the orange cation of formula.

VIII



$\lambda_{max.}$ 480m.μ.[202]

Fuschsondimethylimmonium ion

An attempt was made to isolate complexes of these protonated dye cations. Such complexes are precipitated as orange-red products from conc. HCl solutions. In some cases, the colour of these compounds has been observed to change to brown and ultimately to dark green on keeping the dried complexes for a long time. We attribute these changes to loss of hydrogen chloride. The complexes are decomposed by moisture, acetone and alcohol.

Attempts to prepare protonated dye chlorides, by reacting the dyestuff with anhydrous HCl on a vacuum line, were not successful. The dyestuff partially dissolved in liquid hydrogen chloride giving an orange solution but on removal of excess of hydrogen chloride the starting dyestuff was obtained. The unstability of the protonated dyestuff chlorides is possibly because of the anion (HCl_2^-) being not of strongly acidic character. Two types of the dyestuff complexes were prepared in the course of the present work.

(i) Heteropoly acid complexes

(ii) Lewis acid complexes.

(i) Heteropoly acid complexes were obtained as orange-red precipitates by mixing the solutions of the dyestuffs and heteropoly acids in about 6N hydrochloric acid. The products gave a negligible test for chlorine. The determinations of non-volatile residue (See Table 7) in the

heteropoly acid complexes show that all of these compounds contain 2:1 ratio of protonated dye cation to heteropoly anion. However, as the products were rapidly decomposed by moisture, reliable carbon and hydrogen analysis could not be obtained to confirm the stoichiometric composition of these compounds.

Reflectance spectra:- The absorption spectra of carbonium ions in acid solutions has previously been studied by Lewis and Bigeleisen[183] and other workers[181, 199]. The crystal violet ion absorbs at λmax. 590 m.μ. in the visible region and on gradual addition of an acid the chief absorption (when one of the NMe_2 group is protonated) first moves towards the red(λmax. 630 m.μ.) and then (when second NMe_2 is protonated) towards the violet part of the spectrum. In the presence of excess of acid, the carbonium ion dyestuffs show[181,183] a broad absorption band at shorter wavelength. For example, doubly protonated crystal violet cation absorbs at 470 m.μ. (cf. structure VIII).

The reflectance spectra of the solid heteropoly acid complexes precipitated from concentrated hydrochloric acid are shown in Table 5.

(ii) Lewis acid complexes:- Triphenyl carbonium ion complexes of a series of complex halo-anions have been studied[200] in aceto-nitrile solutions. New derivatives of malachite green, brilliant green and crystal violet have

been found, in the present work, to be formed by reaction between the dyestuff chloride and Lewis acid in concentrated hydrochloric acid. Orange-yellow products were obtained with $SnCl_4$, $SbCl_5$, $PbCl_4$ and $FeCl_3$. These compounds are almost insoluble in concentrated hydrochloric acid but are apparently soluble in the presence of excess of complex halo acids. From the infrared and visible absorption spectra, it is concluded that all these salts contain protonated dye cations, similar to the heteropoly acid complexes precipitated from concentrated hydrochloric acid, and complex haloanions of the type $SnCl_6^{-2}$, $SbCl_6^{-1}$, $PbCl_6^{-2}$, $FeCl_4^{-1}$. The complexes give a blue solution in acetone which is probably due to a reversible species formed due to partial solvation of the multicharged dye cations, as the evaporation of the solvent again gave yellow coloured products. Attempts were made to prepare the dyestuff salts with $AlCl_3$, $HgCl_2$, $TiCl_4$ and $ZrCl_4$ but no complex was precipitated out from acid solutions probably due to the more easily hydrolysable nature of the complex halo-anions.

Reflectance spectra:- The reflectance spectra of the protonated dye cation with the complex halo-anion are characteristic for protonated dyestuff cations. (cf. reflectance spectra of heteropolyacid complexes) The details of the spectra are given in Table 6.

Table 5 Reflectance spectra of heteropoly acid complexes precipitated from conc. HCl.

Protonated Dyestuff	Malachite Green	Brilliant Green	Crystal violet
Silicotungstate	475b, 640	470b, 640	475b, 655
Ferritungstate	470b, 645	475b, 645	460b, 660
Zincitungstate	475b, 640	475b, 640	465b, 655

Major peaks are underlined.

Table 6 Reflectance spectra (400-700 m.μ.)

Protonated Dyestuff	Malachite Green	Brilliant Green	Crystal violet
$SnCl_4$ complex	460b, 640	465b, 645	450b, 645
$SbCl_5$ complex	480b, 630	474b, 650	490b, 640
$FeCl_3$ complex	440, 620		

Infrared spectra of the complexes precipitated from concentrated hydrochloric acid.

The spectra of the protonated dyestuff complexes with heteropoly acids and complex haloanions are similar to the spectra of unprotonated carbonium ion dyestuffs except for minor changes due to protonation of the nitrogen atoms of the dyestuff cation. From the infrared evidence, it is

concluded that protonation does not change the overall symmetry of the dye cations.

Experimental

Lead tetrachloride was prepared by dissolving lead dioxide in ice cold hydrochloric acid. The solution was filtered and used as such for further reactions. The yellow solution containing $PbCl_6^{-2}$ ions.

Other chemicals used were laboratory reagents and were used without any further purification.

Preparation of Complexes:- The carbonium dyestuffs and heteropoly acids or the other metallic chlorides were dissolved in concentrated hydrochloric acid and the solutions were mixed after filtration. On mixing the two solutions, orange-yellow or orange-red products separated out and were filtered off and dried under vacuum.

Estimation of non-volatile components was carried out by ignition as described in section C of this chapter.

Estimation of Chlorine:- The dyestuff salts of complex halo-anions were decomposed by boiling with sodium hydroxide solution. The solution was filtered and chlorine was estimated as AgCl by the usual procedure.

The carbon and hydrogen analyses and percentage of non-volatile components are given in Table 7 for the protonated dyestuff complexes with heteropoly acids. For

Table 7 Analysis Results of Protonated Carbonium Dye Complexes:

Protonated dye complex	Non-volatile component Found%	Non-volatile component Theory%	Found C%	Found H%	Theory C%	Theory H%	Dye : Anion
M.G. Tungstosilicate	80.62	80.41	15.02	1.53	15.36	1.61	2:1
B.G. Tungstosilicate	74.54	74.63	18.43	2.08	17.77	1.86	2:1
C.V. "	78.91	78.51	13.08	1.72	16.56	1.76	2:1
M.G. Tungstoferrate	76.97	76.83	15.47	2.02	15.48	1.55	2:1
B.G. "	76.08	76.02	11.43	2.07	17.61	1.93	2:1
C.V. "	78.08	78.05	17.48	2.38	16.43	1.75	2:1
M.G. Tungstozincate	78.94	79.11	13.51	1.95	15.98	1.97	2:1
B.G. "	74.81	74.74	16.94	2.48	16.89	2.29	2:1
C.V. "	78.25	79.84	11.02	1.86	16.39	1.74	2:1

the complex halo-anion complexes, the chlorine analysis was carried out immediately after preparing the complexes and the stoichiometries derived from these results are given in Table 8.

Infrared spectra were recorded in Nujol and hexachlorobutadiene mulls.

Table 8

Protonated Dyestuff Complex	Found Cl%	Calc. Cl%	Dyecation:anion
M.G. $SbCl_5$	40.98 40.38	40.55	1:2
B.G. $SbCl_5$	39.96 39.40 38.52	38.32	1:2
C.V. $SbCl_5$	43.63 43.73 40.65	43.51	1:3

F. Preparation of some Lewis acid-dyestuff complexes.

The phenomenon of the addition of Lewis acids (similar to Brönsted acids) to basic dyestuffs has been known since 1908. Meyer[201] showed that basic dyestuffs give the same absorption spectra when dissolved in concentrated sulphuric acid or in a solution of stannic chloride in chloroform. In the first case H^+ is added to the basic group of the dyestuff and in the second case a $SnCl_4$ molecule is added to the dyestuff. Later Lewis and Bigeleisen[183] studied the absorption spectra of methylene blue in a methyl cyanide solution of 0.1M stannic chloride and in 3M sulphuric acid. In both cases, the spectra were found to be the same. They attributed this similarity to the formation of $D_1(SnCl_4)^+$ and $D_1(H^+)^+$ cations. The formation of $D_1(SnCl_4)^+$ was not proven, as a slight hydrolysis of $SnCl_4$ will produce HCl and the observed spectra may be due to the formation of $D_1(H^+)^+$ cations instead of $D_1(SnCl_4)^+$ ions (cf. formation of $D_1(H^+)$ cations in conc. sulphuric acid). It was later found[183] that even if the greater part of stannic chloride had been converted into hydrochloric acid, there would not be enough of the latter to change D^+ into $D_1(H^+)^+$, as it requires at least 1M hydrochloric acid in methyl cyanide solution to eliminate the D^+ band and to form the $D_1(H^+)^+$ cation.

More recently, Gutmann[202] has shown that the absorption

spectra of crystal violet in $POCl_3$ are the same in the presence of $SnCl_4$ or $SbCl_5$. The colour changes with addition of Lewis acids were attributed to the successive addition of the accepter chloride molecules to $-NMe_2$ groups. The first addition gives a green colour and the second addition produces an orange yellow solution (cf. Colour changes of crystal violet in hydrochloric acid).

In the present work it was proposed to prepare a new series of the dyestuff derivatives with $SnCl_4$ and $SbCl_5$ by working in a non aqueous medium. Malachite green, brilliant green and crystal violet react with Lewis acids ($SnCl_4$ and $SbCl_5$) in anhydrous methylene chloride and orange red adducts are precipitated out. These products give blue or green solutions in acetone which give orange red products on removal of the solvent and are slowly decomposed by moisture. Some of the products are slightly soluble in methylene chloride and solution spectra were recorded. The details of the absorption data are as follows in Table 9.

The solution spectra show that the absorption bands are similar to those of the reflectance spectra of the dyestuff complexes prepared in concentrated hydrochloric acid (see Table 5). This close similarity indicates complex formation at the nitrogen atom.

The analysis results were inconsistent and it is

Table 9 Solution spectra of Lewis acid complexes in methylene chloride (400-700 m.μ.).

Dyestuff	Malachite green	Brilliant green	Crystal violet
$SnCl_4$ complex	468b	-	insoluble
$SbCl_5$ complex	465,622	645b,630	insoluble

apparent that there are differing amounts of Lewis acid co-ordination and these products are mixtures of different species. Lewis and Bigeleisen[183] have determined the ratios of different protonated species formed with hydrochloric acid and stannic chloride in methyl cyanide solutions. The ratios are

$$\frac{D(H^+)^+}{D(2H^+)^+} = .033$$

(D = Capri Blue)

$$\frac{D(SnCl_4)^+}{D(2SnCl_4)^+} = .13$$

It is clear that in the latter case the ratio is much larger and the proportion of the lower species formed in the case of Lewis acid is greater than in the protonated complexes.

In view of these difficulties it was proposed to prepare compounds with different stoichiometric compositions by reacting equivalent proportions of Lewis acids and the

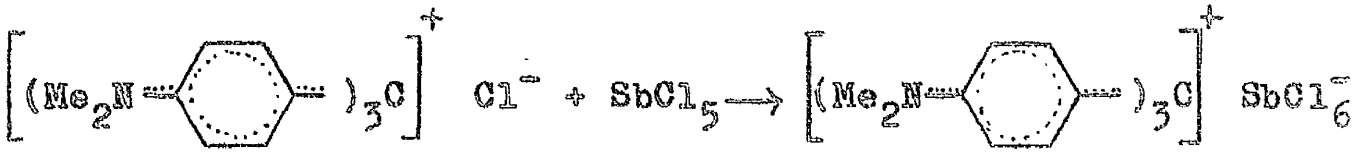
dyestuffs in methylene chloride solution in order to isolate discrete adducts. Crystal violet complexes with different quantities of antimony pentachloride were prepared and the reflectance spectra were recorded as shown in Table 10.

Table 10

Reflectance spectra of crystal violet-antimony pentachloride complexes.(400-700 m.μ.)

Compound	Colour	Absorption bands in m.μ.
Crystal violet chloride	viotel	600 broad
C.V.:$SbCl_5$ 1:1	violet	600 broad
1:1.5	dark green	450, 595 broad
1:2	green	440, 495, 650
Complex precipitated in excess of $SbCl_5$	orange red	420 broad, 640

The absorption spectrum of the 1:1 complex is identical with that of the parent dyestuff. It seems that the first addition of $SbCl_5$ molecule forms a complex halo-anion. The reaction may be represented as follows.

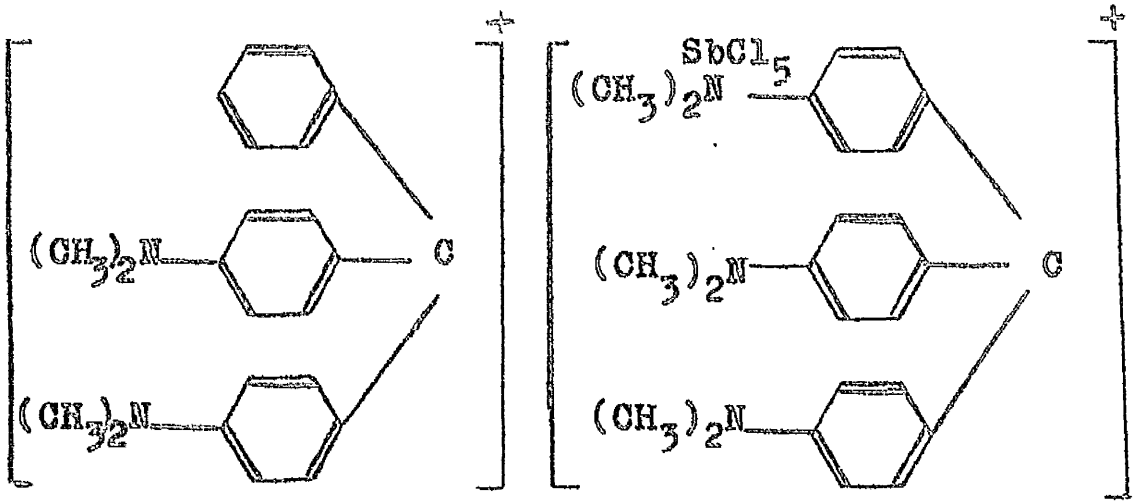


violet
λ_{max} 600 m.μ.

violet
λ_{max} 600 m.μ.

The formation of $SbCl_6^-$ ion has been confirmed by studying the far infrared spectra of the 1:1 adduct and other complexes. These compounds show a strong intensity band at 340 cm^{-1} which has been attributed to $SbCl_6^-$ ion.
[cf. NO^+ $SbCl_6^-$ absorbs at 345 cm^{-1}(61)]

The spectrum of 1:1.5 complex indicates the appearence of a weak band at 450 m.μ. This shows that the crystal violet cation has been partially converted to the malachite green like structure as one of the $-NMe_2$ groups is co-ordinated with $SbCl_5$. In 1:2 complex the formation of the cation X is expected to be formed by a

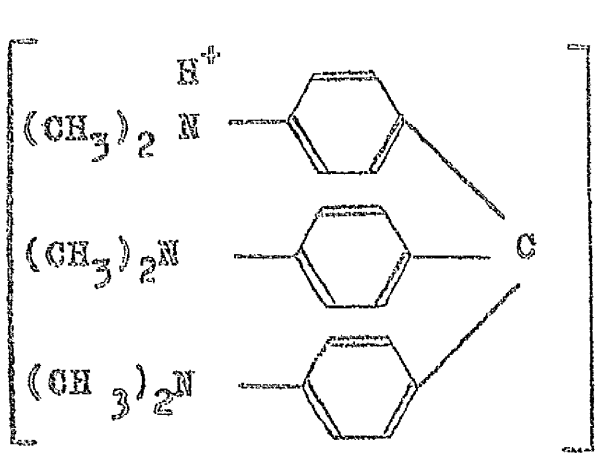


IX

X

$\lambda_{max.}$ 430, 625m.μ.[183]

$\lambda_{max.}$ 440, 495, 650m.μ.



$\lambda_{max.}$ 437, 635m.μ.[204]

XI

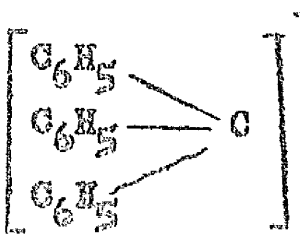
simple reaction.

$$C.V.^{+}Cl^{-} + 2SbCl_5 \longrightarrow C.V.(SbCl_5)^{+} \quad SbCl_6^{-}$$

X

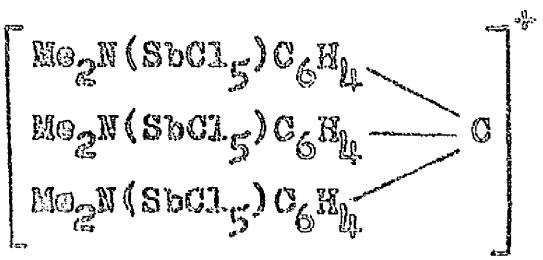
The appearence of a new peak at 495 m.μ. in compound X suggests that another species is formed which probably involves co-ordination with the second NMe_2 group of the cation. The structures IX and XI are given for comparison of their absorption data with that of the Structure X.

The absorption band at 420 m.μ. in the spectrum of the orange-red product prepared in an excess of $SbCl_5$ indicates the formation of C.V. $(SbCl_5)_3^{+}$ cation, as the other cations with similar structures absorb in the same region.



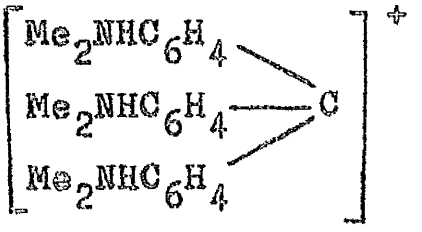
XII

triphenylcarbonium ion
$\lambda_{max.}$ 425m.μ. [203].



XIII

fully co-ordinated crystal violet ion.
$\lambda_{max.}$ 420, 640m.μ.



XIV

fully protonated crystal violet ion.

$\lambda_{max.}$ 423m.μ. [204]

The presence of the weak band at 640m.μ. indicates that other species containing a lesser number of $SbCl_5$ molecules, for example species X, are also present in this product. These findings are in agreement with the recent work of Gutmann[202], who has described the formation of $C.V.(SbCl_5)_3^+$ cation (structure XIII) by a reversible reaction in $POCl_3$ solution in presence of excess of the Lewis acid.

Experimental

Antimony pentachloride was freshly distilled before use and was handled in a dry box.

Methylene chloride was distilled over activated molecular seive and was stored under dry conditions.

The dyestuff complexes were prepared by mixing the proportional amounts of the dyestuff and antimoney pentachloride in methylene chloride solutions. The reactions were carried out in a dry box. After mixing the reactants, the solvent was removed on a vacuum line and chloride

analysis were carried out immediately after preparing the complexes. The chlorine analysis are given below.

Complex crystal violet : $SbCl_5$	Found Cl%	Calc.Cl%
1:1	30.114	30.137
1:1.5	36.85	35.23
1:2	39.02	38.82

Infrared spectra. All the compounds with different proportions of dyestuff / $SbCl_5$ complexes show similar spectra in the 2-50 μ. region. The spectra are characteristic of the crystal violet cation. With the increasing proportion of $SbCl_5$ in these complexes, the infrared spectra showed slight changes, especially in the complex precipitated in an excess of $SbCl_5$. These changes are attributed to the co-ordination of the Lewis acid to the $-\ddot{N}Me_2$ groups of the dye cation. From the close resemblances, shown by complexes of different ratios, it is concluded that the overall structure of the dyestuff cation remains the same. The absorption band at 340cm^{-1} has been assigned to $SbCl_6^-$ ion. The spectra were recorded in Nujol and hexachlorobutadiene mulls. Details of the infrared data are shown below:

Complex	Absorption frequencies cm^{-1}.
Crystal violet:$SbCl_5$	
1 : 1	1585s, 1471m, 1351s, 1290w, 1233w, 1190sh, 1164s, 1124sh, 1064w, 943s, 917m, 833s, 800w, 763m, 746m, 729s, 613w, 555m, 513s, 420s, 340vs,b. ($SbCl_6^-$).
1 : 1.5	1587s, 1481m, 1351s, 1295w, 1232w, 1190sh, 1164vs, 1124sh, 1022w, 943s, 916s, 833s, 793w, 763w, 746w, 725s, 614w, 555w, 526w, 417s, 335vs.b. ($SbCl_6^-$) .
1 : 2	1587s, 1481m, 1408w, 1360s, 1221w, 1190sh, 1175vs, 1136w, 1020w, 943m, 910s, 833s, 793w, 763w, 740sh, 722s.
Complex precipitated in excess of $SbCl_5$	4348w, 1613s, 1572s, 1504w, 1453m, 1418w, 1370w, 1310w, 1252w, 1212m, 1060w, 1136m, 1124m, 1042m, 1010w, 970w, 940w, 885w, 840s, 787m, 769w, 735w, 720m.

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